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Chem. & Phys.
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The Journal of Industrial and Engineering Chemistry

PUBLISHED BY

The American Chemical Society

VOLUME XIV, 1922

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The Journal of
INDUSTRIAL & ENGINEERING CHEMISTRY
Published Monthly by The American Chemical Society

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Volume 14 JANUARY 1, 1922 No. 1

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EDITORIALS

Pull Together

The JOURNAL now enters a new era of opportunities and responsibilities. For a time at least, while chemical and general industry remains stationary, there is likely to be less development of facilities for industrial research than can be considered desirable or perhaps necessary in view of all the facts. With the compelling force of war removed it will be more necessary than ever to keep in view the future of chemical industry in America and to use all the great influence of our SOCIETY and JOURNAL to the end that necessary research and cordial governmental coöperation with chemical industries essential to both peace and defense be not relinquished. That Mr. Howe, our new editor, with the aid and backing of the SOCIETY, can and will carry out to its completion the program of work already so ably begun is assured. In accomplishing his task he has the cordial good wishes of all of us.

W. D. RICHARDSON

What of Chemical Industry?

The tide of the great war was turned the day that necessity drove the Allies to coördinated effort, and forced upon them a policy of coöperation under a single commander with full power. A machine without coördination of moving parts is junk; a business enterprise not well coördinated is advancing to meet the sheriff, and a regiment of men not trained in coördination of action is simply a mob; yet it took the allied nations three years' time and a near-defeat to see that national and world problems are governed by simple home-known rules.

American Chemical Industry is being hard pressed these days. Foreign competition, tariff delay, governmental regulation, labor, freight and fuel costs, foreign exchange, all seem to be wonderfully organized and perfectly coördinated under the unified command of General Business Depression, with headquarters somewhere in the U. S. A. American Chemical Industry has lost much ground in the fight against the General and the divisions he has marshaled with such uncanny skill, largely because they have not seen the light of full and complete coördination of effort even as the Allies did.

Is it not about time for American Chemical Industry to lay aside localisms, party politics, commercial smoke screens or whatever it is that stands in the way, and come out in the open, as the Allies finally had to do, consolidate the whole interest into a common battle line, unify the command, appoint a Commander-in-Chief with power, and settle the question here and now in 1922, as to whether or not we are going to have a real American Chemical Industry?

M. C. WHITAKER

Stand behind the Editor

With this issue, a new hand guides the policies of THIS JOURNAL. Upon the shoulders of the Editor falls the responsibility for reflecting the sentiment of the more than 15,000 members of the AMERICAN CHEMICAL SOCIETY. His is the voice which speaks the opinion of the chemists of this country, whether it pertain to matters of professional interest, to the country's economic and industrial welfare, or to patriotic response to the Nation's need. There is no way by which the Editor can better feel the pulse of the SOCIETY than by direct communication with its members, individually or through the collective groups in the Local Sections. Write to the Editor with every constructive suggestion you can offer for the improvement of THIS JOURNAL. Such letters have come to the Editor's desk all too seldom. Again, the readers make the atmosphere which leads firms to seek the advertising pages. Mention THIS JOURNAL when corresponding with advertisers, present or prospective.

It is a physical impossibility for the Editor personally to cover all fields necessary to keep the pages alive and up-to-date. Individual members can be of great assistance to the Editor in locating hidden mines of information. It is to be hoped the day will soon arrive when the SOCIETY'S financial condition will justify the addition to the editorial staff of an adequate field force.

Speaking out of the abundance of five years' experience, I would urge that the members of the SOCIETY, individually and collectively, stand dynamically behind the incoming Editor. Energetic coöperation will make THIS JOURNAL hum.

CHAS. H. HERTY

Howdy

Fellow chemist, please meet the new Editor! And before you read further turn back to page 2 of THIS JOURNAL for 1917 and look again at Dr. Herty's "By Way of Introduction." He has come near his mark. May we come as near ours.

We conceive our work to be that of helping to advance technical chemistry, to aid chemical industry and all industry by espousing the cause of scientific and industrial research (if there is a difference), and to create a proper appreciation and understanding of chemistry among our nonchemical people. We must keep in mind the average man, whether it be in the articles we accept or any work performed. We must never forget that progress depends upon fundamental research and that it is from industry that we derive support vital for such research. To coöperation we must add correlation and coördination.

While we have been reminded that we have more than 15,000 bosses who cannot be pleased simultaneously, we prefer to count on more than 15,000 helpers. We are stockholders together in this enterprise. This is *Your* journal. The Editor wants your frank opinion, suggestive or unfavorable, as it may be. We hope to hear policies and needs discussed in various Local Sections as was so successfully done by the New York Section December 9.

We chemists still have a deal of work to do. We can do it together. Let's go.

The Staff

The Directors have been able to appropriate a modest sum for an Associate Editor who is to be appointed. His headquarters will be in New York City, and he will devote himself to plant and field in an effort to build up the technological side of the JOURNAL. This addition to the staff has long been desired and is sure to add strength. The Assistant to the Editor, Miss N. A. Parkinson, is thoroughly experienced, and comes to us from the *Journal of the Association of Official Agricultural Chemists*, where she has been Associate Editor. Miss Thomas, Miss Reynolds, and Miss Gordon will continue their valuable work.

The new headquarters will be 810 Eighteenth Street, N. W., Washington, D. C. Here we shall be easily accessible by whatever route you travel in the city.

"Come in, rain or shine."

Appreciation and a Wish

It is really remarkable how our Society has grown and how it has become a potent factor in everyday life.

In quietly going over its several publications evidence appears that it is interested not only in pure science, but in the application of the principles of the science to all industries dependent upon such principles.

One must feel proud of the splendid contributions which fill the pages of the *Journal of the American Chemical Society*, and one must also recognize the worth-while things appearing in the *Journal of Industrial and Engineering Chemistry*. The contributions to the latter Journal are most helpful to the great rank and file of American chemists, who are giving, in a very unselfish way, their best efforts to the establishment of industries in the home land, a goal to which American chemists have aspired since the founding of the Republic.

> *This people of Washington and Lincoln are conquering the difficult problems of to-day, no less worthily, and with the faith and confidence which they bequeathed to us. We are sure to find the ways to restored prosperity and our meed of happiness.*—Warren G. Harding.
>
> * * *
>
> The above message is the first ever signed by a President of the United States for billboard purposes. It is being used in a prosperity campaign by the International Association of Rotary Clubs.

Again, *Chemical Abstracts* must appeal to every member of the Society. It has meant very much to me in my own work. It has directed me to hundreds of papers which, perhaps, would have escaped my attention, or which I would have discovered only after long, tedious search.

One of the happiest moments I have had during the past year was when it was determined to institute a section on Chemical Education. Our teachers deserve the very best that can be provided. Most of them are also investigators, heroically devoting themselves to instilling the principles of chemistry into the minds of vast student bodies destined for future industrial activity. Much of this noble work is being done under most unsatisfactory conditions. The first meeting of teachers of chemistry, in New York last September, showed clearly how eager they were to be of service in this fundamental preparation and to make sacrifice for the best interests of chemistry throughout the land.

I can't refrain from expressing the wish that as all the many interests, represented in the great membership of the Society, are working for the upbuilding of American chemical industries, sight will not be lost of the fact that reciprocity is only fair; and that the industries as they arise, develop, and succeed, shall see to it that ample means are provided for research in pure science, for the erection of laboratories, for the maintenance of a well qualified group of experimenters, and last but not least, for the payment of adequate salaries to our self-sacrificing teachers, that they may be easy in mind and able to throw themselves wholeheartedly into their particular occupation.

There is no reason at all why such should not be the case; and it ought to be our purpose to acquaint our neighbors of the great laity as to what chemical science is, how closely it comes to every man, woman and child of our country, how its pursuit is, in the end, their happiness and comfort, and that they should be supporters and benefactors of a profession of which it is an honor to be a part.

The achievements in publication and in other directions have been due largely to the loyal support given the Society. Continued support may be counted upon to accomplish our future tasks.

Edgar F. Smith

Distinguished Service

Five years ago, on January the first, 1917, Dr. Chas. H. Herty entered upon his duties as editor of This Journal. They have been years of great events in the world at large and years of extraordinary activity in the field of our profession. During all this period of development and stress the *Journal of Industrial and Engineering Chemistry* under Dr. Herty's guidance has faithfully reflected the advances in the applications of chemistry, to industry and warfare, which have so profoundly influenced both. But it has done much more. It has voiced in aggressive and convincing editorials the sound Americanism of the chemists of the country. It has consolidated opinion. It has made clear to all who would read the close relationship between the chemical industries and national prosperity and defense.

To reach a wider audience and extend the influence of the Society Dr. Herty established the News Service, through which, with the cordial coöperation of the press, the notable advances in chemistry have been placed before the public and their bearing upon the affairs of the community made manifest. To this Service the present general recognition of the vital significance of chemical science is largely due.

In pursuance of his clearly defined policy of establishing American chemistry in its true relation to practical affairs, Dr. Herty developed a singular aptitude for the presentation of its claims before Congressional Committees and public bodies. He convinced by the cogency of his facts, persuaded by the charm of his personality, and inspired by the splendid courage of his convictions.

The influence of Dr. Herty as an educator, his efficiency as an administrator when president of the Society, and his distinguished success an an editor were due not only to his chemical scholarship, but in large measure to his exceptional personal quality. He combines the courtesy of the Southern gentleman with the aggressiveness of the crusader. His remarkably wide acquaintance is a working asset of the utmost value, for he has a habit of converting acquaintances to friends.

For many years Dr. Herty has been an outstanding figure in the American Chemical Society. Few, if any, have served it more variously and effectively. He has earned and carries with him to his new environment the gratitude and good wishes of the chemists of America.

A. D. Little

Do You Remember?

It seems only a few days ago that we were being urged to make America independent in essentials and the then Secretary of the Interior was urging men to "rediscover America." Among other things we wanted a potash industry. We wanted it so badly that every source was sought and tried. The Government experimented with kelp, we heard much of feldspar, of greensands, of alunite, of natural lakes, and of California deposits. Progress was made, millions were spent, and some research and chemical engineering of a high order performed. Chemists and investors knew something of the competition to be met when normal times returned, but they counted on Americans meaning what they said when they clamored for a potash industry.

So research was recognized as the key to the situation—purer product at lower cost. In one large plant, if we take the cost per unit of K_2O during the first four months of 1919 as 100 per cent, it was 58.3 per cent for the same period of 1920 and in 1921, 32.6 per cent. Quality was assured. Production ran into thousands of tons although the inspired daily press articles would have you believe there can be no American potash industry. To have a potash industry there must be a market for potash.

Before us is a copy of the contract between "The American Agricultural Chemical Company and others with Deutsches Kalisyndikat, G. m. b. H.," dated September 28, 1921. The full list of buyers who are parties of the second part follows:

The American Agricultural Chemical Company
Virginia-Carolina Chemical Company
International Agricultural Corporation
Armour Fertilizer Works
Swift & Company
F. S. Royster Guano Company
Arkansas Fertilizer Company
Baugh & Sons Company
Berkshire Fertilizer Company
Caraleigh Phosphate & Fertilizer Company
Darling & Company
E. Rauh & Sons Company
Federal Chemical Company
F. W. Tunnell & Company
Georgia Fertilizer & Oil Company
G. Ober & Sons Company
Griffith & Boyd Company
Gulf Fertilizer Company
I. P. Thomas & Son Company
Miller Fertilizer Company
Mutual Fertilizer Company
Olds & Whipple
Piedmont-Mt. Airy Guano Company
Read Phosphate Company
Reliance Fertilizer Company
Richmond Guano Company
Robertson Fertilizer Company, Inc.
Rogers & Hubbard Company
Smith Agricultural Chemical Company
Southern Fertilizer & Chemical Company
W. B. Tilghman Company, Inc.
Wuichet Fertilizer Company
Wilson & Toomer Fertilizer Company
York Chemical Works

These firms agree to purchase at least 75 per cent of their requirements on this contract, this amount, 35,680 tons, being lumped together to obtain extra quantity discounts. The contract is too long to reprint. We quote:

> 1—Such participant shall state in its price lists that Potash can now be had in all required quantities, and that it is advisable to buy mixed goods containing as high a percentage of Potash as is suitable to the respective crops; and
>
> 2—Such participant shall instruct its selling organization and salesmen to sell and recommend mixed goods containing as high a percentage of Potash as is suitable to the respective crops.

Such coöperation is rewarded by an extra discount!

And as for anti-dumping:

> Seller hereby also assumes and agrees to pay any tax or duty affecting deliveries under this contract which may be imposed or assessed by the United States Government under the Anti-Dumping Act of 1921 or any amendment thereto which may be hereafter enacted provided however in case of such amendment Seller shall not be required to pay any tax or duty in excess of amount of tax payable under existing provisions.

Now what of the remaining 25 per cent, an amount which our industry *can* supply? Bids were asked November 14 to be made within a week. November 16, American potash was offered to meet any foreign quotation, even though that meant a loss to the producers. The reply came that if the bid had been made a few days before things might have been different but contracts had already been made with French interests. Do we want an American industry? We would like to know more about the factors at work and whatever other side there may be to this transaction.

Meanwhile research goes forward even though the warehouses are full of American potash which Americans refuse to purchase. Do we want the industry?

Creating Good Will

In the *Journal of Commerce*, New York, issue of December 2, there appears the following paragraph under the caption "A. C. S. Not a Mendicant:"

> It is refreshing to find one organization which can hold its convention and practically pay its own way and which at the same time is willing to do so. The usual thing in conventions is for the committee on arrangements to solicit as much money from the business men of the community as is humanly possible, spend whatever part of it is necessary and talk of refunding the balance pro rata. Somehow these refunds are never made. The recent convention of the American Chemical Society furnished the refreshing contrast to this attitude on the part of societies and organizations in general. Plans were early matured by the committee in charge calling for the payment of as great a proportion of the expenses of the meeting by the members themselves as possible. It was, of course, necessary to do some soliciting of funds. So successful were the efforts of the committee, however, that the society was able to pay approximately 80 per cent of its own expenses. The really remarkable thing, however, was the handling of the surplus. Pro rata return of all funds remaining after the payment of expenses was made to the firms who contributed. About 40 per cent of the solicited funds were returned in this way. Is it any wonder that many cities compete for the honor of the American Chemical Society meeting?

Of course the *Journal* did not appreciate that on several occasions Local Sections of the SOCIETY have been equally successful in managing national conventions. People generally are finding that many chemists are good managers and that when a Section of the SOCIETY undertakes a project of this sort it is put through on a sound business basis.

Who Will Be Next?

In these days when an honest effort is being made to bring about an era of brotherly love, we would like to believe that after all our bitter lessons we have reached a point where there can be straightforward dealing and fair, stimulating competition for such business as the world affords. But we are rudely shaken by the following official report and made to realize anew that "eternal vigilance is the price of safety."

We reproduce the document in its entirety from *Idea Nazionale* of August 28, 1921.

> No. 1784. General Private GERMAN EMBASSY AT ROME
>
> Rome, 25th May 1921
>
> TO THE MINISTER FOR
> FOREIGN AFFAIRS,
> BERLIN.
>
> I reply to the invitation contained in Circular of 13th May to all commercial attachés, to report to your Ministry as to the situation, and our activity and our commercial development abroad, and I have the honor to report as follows:
>
> The figures of German commerce in Italy show that after the Armistice our traders were not inactive in reconquering the Italian market compared with France, England and the United States and maintaining our supremacy, but that does not mean that we have reached the state of your circulars of 20.8.1920 and 29.8.1920.
>
> In order that we may create for ourselves a favorable political situation, taking advantage of the malcontent of the Italian people, and especially of the Nationalist and Nittian parties against the Powers of the Entente, a political situation which might in due course be favorable to us when Germany should be faced by fresh complications, it is necessary to strengthen this discontent in order to consolidate our situation through economic action.
>
> To this end, the point at which we have arrived is only a quarter of the way. We must create such economic interests and bonds with Italy that whatever happens, Italy will have to follow our political lead.
>
> First of all, it is necessary that a systematic supply of German goods be sent here, even below cost price to a considerable extent. Inundating the Italian market with German goods we will not only have a place sympathetic to Germany, because,

as many of our agents and commercial representatives have verified, Italian consumers gladly accept cheap articles, but we will also create a situation for Italian industry which will render any continuation of activity impossible. This without doubt will cause such a crisis that, besides keeping Italy in constant agitation, will enable us to become the sole masters of the Peninsular trade, the more so as, from our information as to French activity in Italy, it appears that the French fear the outbreak of a revolution here which might cause them similar losses to those suffered in Russia.

The enclosed copy of a report by Sir Capel Cure, British Commercial Attaché, proves that the British too fear the unstable nature of the social situation in Italy.

Further, such situation would enable us to purchase the Italian industries at a very low rate, which would be the key of the situation, since it would also allow us to control trade between Italy and the Balkans in such a way that Italy would not compete with us for those markets (see circular 30th October 1920 regarding Italo-Jugo Slav treaty). This, of course, will happen as soon as Italy is forced to close down.

We have before us a varied field of development in Italian industry, *viz.*, trade in rubber, Fiat, Spa, besides all the tire factories and motor car engine factories which are already in a state of acute crisis on account of the huge German stocks of these lines sent to Italy.

The Siemens Schuckert already approached the Turin companies last September when the factories were occupied by the workmen, but without result. On my advice, the Siemens has already arranged for the absorption of the Fiat through a combination Stinnes-Fiat in the Alpinen and through the purchase by the Deutsche Bank, which has an interest in the Siemens, of the shares which are in the hands of the Banca Commerciale Italiana, amounting to 90,000 Alpinen shares and 100,000 Fiat shares, owned by said Bank. The transaction is on the way to completion, and Messrs. Cavallini, Brunicardi, Trombetti, and Dante are backing it, to whom the Siemens will pay a percentage of $4^1/_2\%$ as was decided at the meeting held in this Embassy in September last. *Then we have the dyeing trade in Italy*, which, though in a precarious state of development, holds the promise of an assured future. It is, however, necessary that, in order to follow out in this branch too the method of peaceful destruction advised by me, the Italian government should not take precautions to prevent the import of coloring matters from abroad, as otherwise it is certain that the Italian industry which, it appears to me, are seeking American capital to support them, might assume a more solid position in the Peninsula, a position which it would be more difficult to destroy.

I have had a promise from the Italian cotton-spinners of the possibility of action on their part against possible provisions of the Italian government. As authorized by you, for my part I have promised that any such action will be compensated by the despatch of textile machines from Germany at very low prices.

It must not be forgotten, however, that the Italian textile industry too offers a field for economic development for Germany in Italy, whether because they are at present going through a period of crisis, or because they obstruct our path towards the East. I understand that in the economic treaties which Italy is on the point of concluding with Jugo Slavia, she demands that the Jugo Slavs shall acquire 200,000 quintales (2000 tons) of textiles per annum in Italy; and it seems that this proposal has been received with pleasure by the Jugo Slavs, since as a matter of fact the Italian cotton-spinners have known how to penetrate that market. Therefore, if we succeed in absorbing part of the Italian cotton industry (I have already made tentative proposals for the Rossi Cotton Mill and for the Prato factory, but up to the present I have had no result, and the negotiations have been passed on to the Schimmelpfeng Agency and to the office of Consul Oster), we could reduce Italian competition in the Balkans, where we could present our product as being Italian.

Then we have the metallurgical industry in Italy, and this is the most important of all since the development which took place during the war is such, that the matter must be taken into serious consideration.

In this connection I will refer to the matter again, pointing out that our participation in the Piombino establishments is assured. Messrs. Cavallini and Brunicardi are taking charge of the question of the Alti Forni (Smelting furnaces) of Porte Ferraio in the interests of the firm of Krupp. They say that at the present moment the owners could ask 210 million lire, but that if the present crisis continues, even half that sum might be sufficient.

Then we have made an offer for the Electric Railway Workshops of Milan, a combination between the Pirelli and Eradania and with the Cotton Transport Corsorzio which could be absorbed, and offers regarding the fleet of Deutsche-Levant Linie, which could become an Italian Navigation Company.

The most important question is in fact that of the control of Italian fuel, which constitutes the integral part of Italian economic life.

The infiltration of the products of the A. E. G. into Italy has destroyed the industry in electrical materials which it will be easy to absorb, the more so as several members of that industry, indicated in my telegram No. 10878, assured me that in view of the business crisis, those Companies seek to obtain foreign capital.

If we assure a supply of electric material on the Italian market, we could obtain contracts for furnishing electric material for several hydro-electric works in construction, and for the State Railways. But it is necessary for the German Companies to understand the necessity of their branches in Italy remaining under the Italian name.

I have entered into agreement for the conclusion of contracts between the A. E. G. Siemens, and the Societa Adriatica of electricity of the group Velpi-Negri for furnishing of the necessary material into the Veneto, that is to say turbo-alternators, turbines, pipes for the waterfall, and all the material, and the furnishing of the material as capital participation of said company, since these supplies are calculated at a value of over eight million lire.

This regarding white fuel.

Then we have at our disposal the Italian wealth of lignite. The Italians do not know how to get the most out of this, and almost treat it as a thing of little value. On the contrary, it is a matter of 300 million tons of which—as I have already reported sub. n. 178 ND—only 3 million tons per annum are used, whilst 115 million tons per year could be got, as the deposits are estimated to be more than 35 meters deep.

Add that by distillation, a thousand tons of mineral oil could be obtained, since lignite has a percentage of 25% of the components of such oil. The deposits of bituminous schist, valued at 115 million tons with 12 and up to 18 per cent of naphtha are worthy of notice, and these two are in a very slightly developed state, which may be attributed to lack of means on the part of the owners.

The Consortium of Chemical Products of Berlin, the Deutsche Bank, and the Discount Gesellschaft are already in treaty with various Italian groups.

As will be seen from this explanation, there is much to do in Italy, but action must be guided by the following rules in order to avoid clashing with Italian susceptibility.

(1) The Deutsche Italienische Vereinig should be able to continue to bring its influence to bear.

Instructions must be given to the Deutsche Italienische Vereinig so that its bulletins shall be inspired to draw attention to the lack of Italian products in Italy, the damage resulting from such lack, and the attempts at economic penetration on the part of foreign countries. Such criterion must also inspire the newspaper campaign of said organization.

(2) The setting up in Milan too of an information office at the Consulate General for Germany with the aim of following the labor movements in North Italy, and to report to Germany in relation to these movements, the necessity to send German material and products in order to increase the crisis.

(3) As to fuel, it is necessary that after the refusal of the Italians of our offer to collaborate in the development of the lignite mines, and for the supply of the market with fuel against facilities of German property which has been so sequestrated, our action shall be turned towards private individuals.

With respectful regards,

The Commercial Councillor
STROHEKER

Now read it again. Note the plan to prevent the development of a chemical industry, first, by making importation of chemicals easy and, second, by purchasing support for this measure with low priced textile machinery. But those who would thus sell themselves are insecure, for there follows a plan for their own "peaceful destruction." Note also that the report is dated May 25, 1921, and not 1914. With such a spirit abroad in the world can we afford to deprive American industry—chemical and otherwise—of any means for defense? Italy, France, and England have adopted strong measures for their industrial defense. We must guard our own.

ORIGINAL PAPERS

A Chemically Controlled Automobile[1]

By George Granger Brown

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The impending shortage of motor fuel and petroleum has been brought forcibly to our attention by a large number of writers within the last few months. Careful estimates indicate that we are probably at the peak of petroleum production and that the production of gasoline in the United States will be unable to exceed the demand for more than five or ten years. At the present time gasoline is selling for nearly $2.00 per American gallon on the continent of Europe, and we may expect an early permanent rise in price in this country.

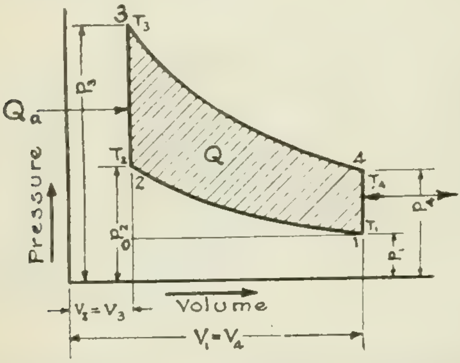

Fig. 1—Ideal Otto Cycle on Pressure-Volume Diagram

It is possible that this shortage may be postponed or temporarily relieved by the development of new sources of raw material, by increasing the yield of oil wells and by more efficient production and handling of gasoline. All these considerations are receiving the attention of chemists and engineers. It is the purpose of this paper to indicate the saving of fuel that may be made by the application of chemical engineering principles to the utilization of gasoline in the automobile engine.

The internal combustion engine, when properly controlled, is a very efficient machine as compared with other prime movers. Its over-all thermal efficiency is then 30 to 35 per cent, but the thermal efficiency of the average automobile is not over 15 per cent. As the Bureau of Mines found that "the combustible gas in the average automobile exhaust from one gallon of gasoline amounts to 30 per cent of the total heat in a gallon of gasoline,"[2] it is evident that the average automobile is wasting in unburned gas alone twice as much energy as it is converting to work.

This loss, entirely preventable by proper control of the mixture, is not only an expensive practice, but a criminal waste of our natural resources. Twenty-five years ago, there were four automobiles in the United States; now there are nine million. Throughout this period fuel has been cheap, and profits large, and the need for carefully controlled combustion has not been felt until very recently. Moreover, the development of the automobile has been essentially mechanical, and naturally the manufacturer has depended almost entirely upon mechanical principles for increased efficiency, overlooking the fact that the combustion of gasoline in an automobile engine is a rather complicated chemical reaction.

Thermal Efficiency

The automobile engine operates on the Otto cycle, shown ideally on the pressure-volume diagram in Fig. 1.[3] The explosive mixture is drawn into the cylinder along the path 0–1. The intake valve closes at 1, and the charge is compressed adiabatically along the path 1–2. It is exploded or burned at constant volume 2–3, giving up the heat of combustion, Q_a, to the products of combustion, which then compose the working mixture instead of the vapor-air mixture. The power stroke (adiabatic expansion) is represented by the path 3–4. The exhaust valve then opens and the gases pass out along 4–1 at constant volume carrying the rejected heat, Q_r, out through the exhaust to the atmosphere. The remaining burned gases are pushed out by the piston along the path 1–0. This completes the cycle, and the heat $Q = Q_a - Q_r$ has been transformed into work represented by the area 1–2–3–4–1. As the efficiency is the ratio of the output over the input:

$$\text{Efficiency} = \frac{Q}{Q_a} = \frac{Q_a - Q_r}{Q_a} = 1 - \frac{Q_r}{Q_a} \tag{1}$$

$$Q_a = WC_v\ (T_3 - T_2)\ \text{heat added} \tag{2}$$

$$Q_r = WC_v\ (T_4 - T_1)\ \text{heat rejected} \tag{3}$$

where W is the weight of charge and C_v the specific heat at constant volume

$$\frac{T_2}{T_3} = \frac{T_1}{T_4} \tag{4}$$

and for adiabatic curves
$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{K-1} \tag{5}$$

$$\text{Efficiency} = 1 - \left(\frac{V_2}{V_1}\right)^{K-1} \tag{1a}$$

$$\text{Efficiency} = 1 - \left(\frac{1}{r}\right)^{K-1} \tag{1b}$$

From thermodynamic reasoning then, the thermal efficiency of the Otto cycle increases with the compression ratio r and with the ratio of specific heats k or $\frac{C_p}{C_v}$. The compression ratio, a mechanical consideration, is fixed by the engine design, and k, the chemical factor, is entirely dependent upon the mixture ratio. From the following list it is evident that high efficiency demands lean or diluted mixtures, *i. e.*, mixtures with an excess of air.

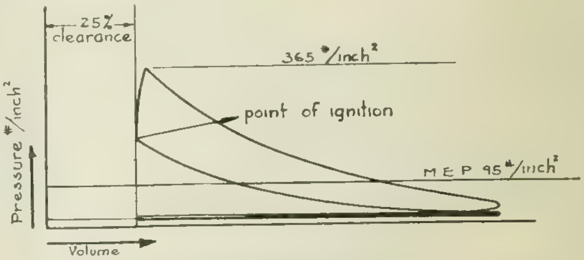

Fig. 2—Average Pressure-Volume Diagram of Otto Engine at Full Load

Gas	K
Oxygen	1.408
Nitrogen	1.408
Carbon dioxide	1.31
Water vapor	1.2
Gasoline vapor	1.1 (approx.)

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] A. C. Fieldner, This Journal, **13** (1921), 57.

[3] A. F. Greiner, *Michigan Technic*, **32** (March 1919).

When the value of k in Equation 1b is taken as 1.408, we obtain the efficiency of the air standard cycle which is used generally as a means of comparison. The measured efficiency of a properly controlled engine is of the order of 62 to 65 per cent of the theoretical air standard. If the measured efficiency be compared with that for an engine working, not upon air, but with the actual gasoline-air mixture employed, as represented in Fig. 2,[3] and if allowance be made for the fact that the specific heat of the gases increases with temperature, a better basis of comparison will be obtained. Compared with this "corrected ideal efficiency" the measured efficiency is of the order of 80 per cent of the theoretical maximum.

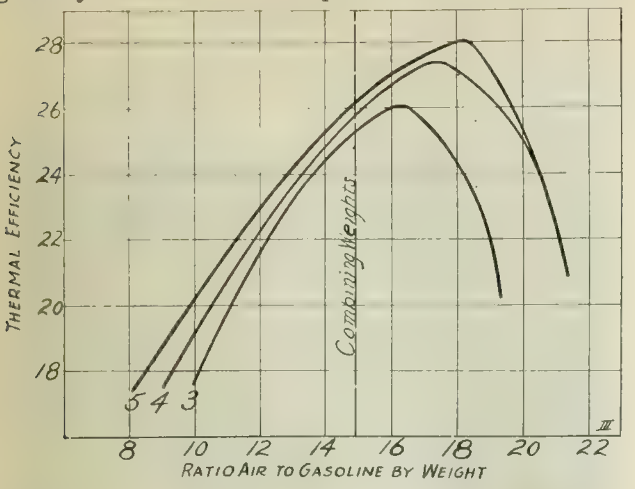

FIG. 3—EFFECT OF MIXTURE CONCENTRATION AND COMPRESSION RATIO (FIGURES AT END OF CURVES) UPON THERMAL EFFICIENCY WITH THROTTLE WIDE OPEN AND ENGINE RUNNING AT CONSTANT SPEED

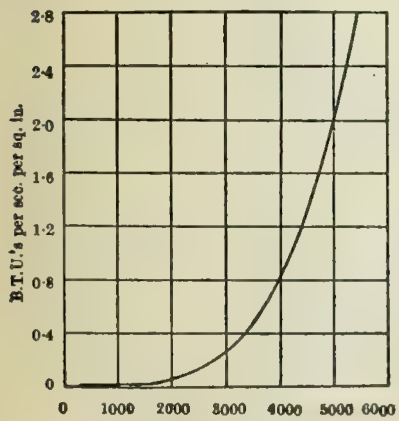

FIG. 4—RADIATION LOSSES

Even if it were possible to eliminate entirely all heat losses in the exhaust and to cooling the water by further mechanical refinements, the increase in efficiency could not exceed 20 per cent. But the efficiency, or miles per gallon, of the average automobile can be practically doubled by proper control of the mixture, or K in the above formula.

The relative importance of compression ratio and mixture proportion is brought out more strikingly in Fig. 3,[4] which shows the influence of these two factors upon the thermal efficiency. The increase in efficiency obtained by higher compression is due to two factors. It gives a relatively longer working stroke, and the increased compression makes for a higher mixture temperature and more rapid explosion.

The high efficiency obtained with dilute or lean mixtures is due to various factors. The lower specific heats make possible the same temperature and pressure increase with a less amount of heat energy. The radiation losses are less from diluted or lean mixtures containing an excess of air because of two factors; the radiation from the diatomic gases is less than that from carbon dioxide and water vapor, and mixtures containing an excess of air develop a lower temperature upon combustion than those containing combining proportions of gasoline and air. This latter statement is made clear by Fig. 4,[5] which shows the amount of heat radiated as dependent upon temperature alone.

REACTION VELOCITY

In order to complete the reaction or in fact to have an explosion at all, the speed of reaction must be at least equal to the rate of heat dissipation; otherwise the heat energy of the spark or of the adjacent gases ignited by the spark will be dissipated before the main body of the charge is raised to the ignition point.

Essentially there are three factors determining the speed of combustion: concentration, temperature, and agitation or turbulence making for more intimate contact. Catalysis is a fourth factor, as is noticed when moisture or steam is present in considerable amount in the explosive mixture. The influence of concentration is best determined by application of the law of mass action. If we write the equation for the combustion of gasoline as follows:

$$C_6H_{14} + 9.5O_2 \longrightarrow 6CO_2 + 7H_2O$$

the velocity of reaction will vary as

$$C_{C_6H_{14}} \times C_{O_2}^{9.5}.$$

If the atmosphere contains a per cent of O_2, and the mixture of maximum velocity contains x per cent by volume of gasoline,

$$C_{C_6H_{14}} \times C_{O_2}^{9.5} = x\left[(100-x)\frac{a}{100}\right]^{9.5} = x\left[(100-x)\right]^{9.5}\left(\frac{a}{100}\right)^{9.5}.$$

Since a is a constant, this expression is a maximum when $x(100-x)^{9.5}$ is a maximum.

In other words, so long as the composition of the atmosphere remains constant, its oxygen content has no influence on the gasoline content giving maximum velocity of reaction so far as the law of mass action is concerned. Then, other conditions being constant, the mixture of maximum reaction velocity will contain exactly the same percentage of gasoline as if the air were pure oxygen, regardless of the per cent of oxygen in the atmosphere.

But the rate of chemical action increases very rapidly with a rise in temperature. Except with certain highly unsaturated hydrocarbons having a negative heat of formation, such as acetylene, the maximum temperature is produced by the mixture containing vapor and oxygen in combining proportions. This factor of maximum temperature will act therefore in opposition to mass action and tend to decrease the

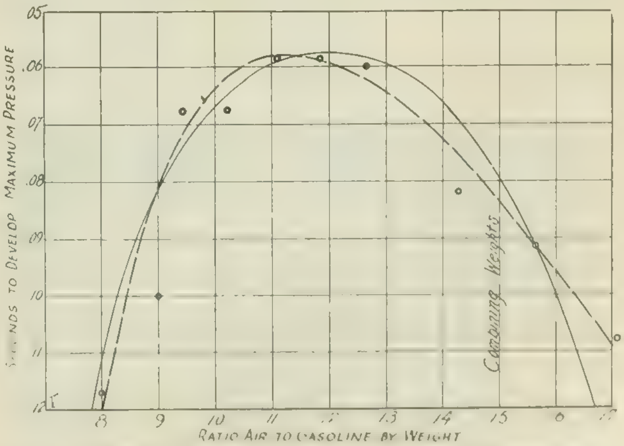

FIG. 5—VELOCITY OF COMBUSTION OF GASOLINE-AIR MIXTURES

excess of gasoline in the mixture of maximum reaction velocity demanded by mass action, to an extent depending upon the cooling effect, or the specific heat of the excess gasoline.

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[4] A. W. Judge, "High Speed Internal Combustion Engines," Pitman & Sons, 1918

[5] A. B. Browne, "Handbook of Carburetion," J. Wiley & Sons, Inc., 1916.

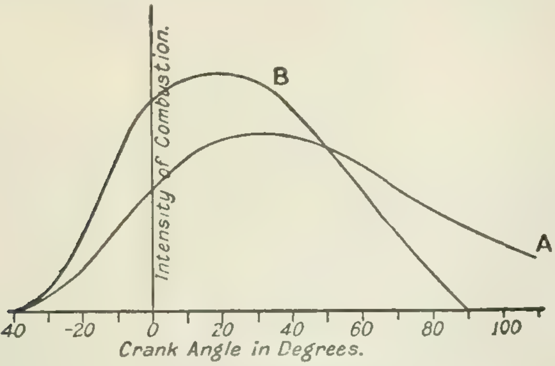

Fig. 6—Intensity and Velocity of Combustion of 12 : 1 and 16 : 1 Air-Gasoline Mixtures

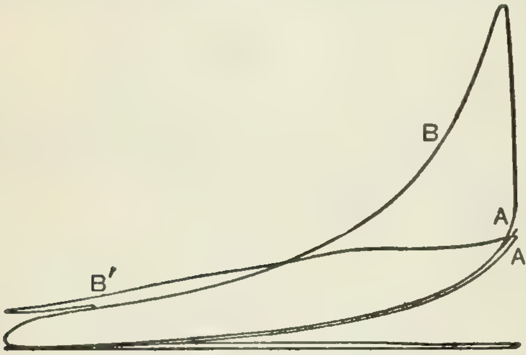

Fig. 7—Indicator Diagram of Turbulent and Quiet Mixtures

But the mixture of maximum reaction velocity of any combustible gas and air has always an excess of the combustible constituent over the combining proportion, due to the influence of mass action, as seen in Fig. 5.[6] Fig. 6[4] shows the more intense and more rapid combustion of a mixture of twelve parts of air (Curve B) over that of a lean mixture of sixteen parts of air (Curve A) as occurs in an engine cylinder, all other conditions being constant.

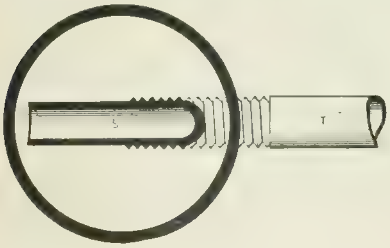

Fig. 8—Sampling Tube in Exhaust Manifold

As an increase in temperature increases the reaction velocity, mixtures otherwise nonexplosive may be exploded if heated. In other words, increasing the temperature widens the limits of explosive mixtures. This fact is of great practical importance.

The mixture of gasoline and air enters the cylinder of the engine at high speed through a comparatively small valve. This velocity of the entering charge agitates the mixture in the cylinder to a greater or less degree, depending upon the shape of the combustion chamber, and the speed of the engine. This agitation or turbulence has a very pronounced effect upon the velocity of combustion. Fig. 7[7] shows the results obtained on an indicator card after two idle compression strokes in which the turbulence was allowed to die down. The curve AB corresponds with normal firing and the expansion line A′B′ corresponds with the second case mentioned, in which all conditions were the same, except decreased turbulence. The ignition periods were 0.037 and 0.092 sec., respectively, or in a ratio of 1 : 2.5.

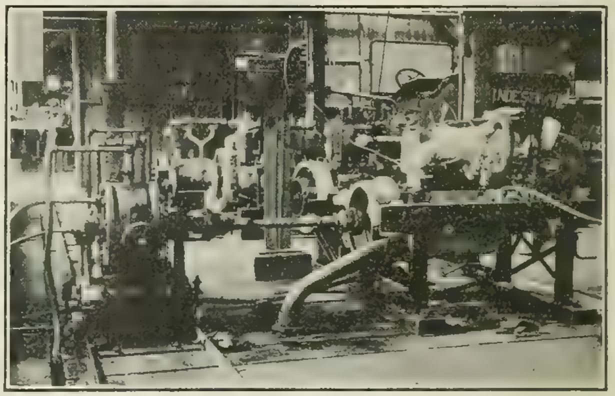

Fig. 9—Engine Set-up in Automobile Laboratory, University of Michigan

Pressure has been found to have practically no influence upon the speed of reaction so long as the temperature remains constant. But increased compression in an engine means increased temperature, for the absolute temperature varies as the absolute pressure in adiabatic processes.

Decomposition

In addition to the complete combustion of gasoline, partial combustion to aldehyde, carbon monoxide, and possibly hydrogen also takes place, along with some decomposition of the hydrocarbon fuel.

The stability of the hydrocarbons is greatest with the lowest paraffin, methane. Ethane is less stable and can be very rapidly decomposed at 1100° C. It has been estimated[8] that at 1500° C., 0.036 sec. is the time required for complete decomposition of the hydrocarbons. At this temperature, which is attained in the gasoline engine, the time of decomposition is of the same order as that of the ignition period.

These two reactions are taking place simultaneously in the cylinder as the mixture is exploded, combustion producing

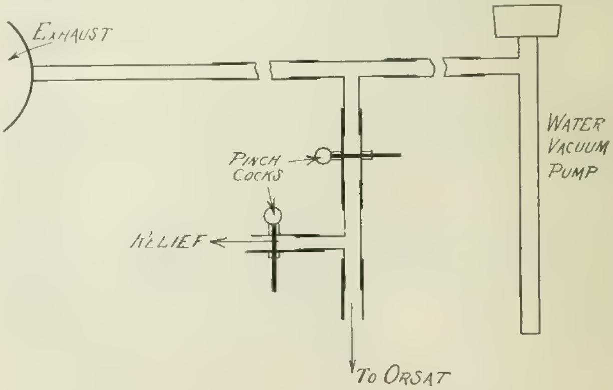

Fig. 10—Connections for Sampling and Analyzing Exhaust Gases

heat and work, and decomposition of the gasoline generally absorbing heat and depositing carbon residue. As decomposition of the fuel takes place much more rapidly at higher temperatures, the lower temperature developed by the combustion of lean mixtures is of advantage in decreasing and eliminating the fuel knock and the deposition of carbon in the cylinders. Dugald Clerk has accomplished the same result by introducing cold exhaust gas into the cylinder charge. This method is more effective in reducing the temperature, but probably not so efficient, owing to the higher specific heat and radiation loss of carbon dioxide over air. Also, it would introduce complications to the design and operation of the engine.

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[6] A. B. Browne, *Loc. cit.* These points are reported as taken from work done at Massachusetts Institute of Technology. The writer of this paper has taken the liberty to suggest another possible curve in a broken line through these same points, as he is of the opinion that the solid line better represents the power developed in an engine with varying mixture proportions.

As is pointed out in this paper, the engine power is a function of the maximum pressure developed and the time at which that pressure is developed in the power stroke. As that mixture developing the greatest temperature increase also develops the greatest pressure, temperature increase has a greater influence upon power developed than it has upon the reaction velocity. Then we should expect to find the maximum power with a mixture containing more nearly combining proportions than the mixture giving maximum reaction velocity.

Compare the curves in Fig. 5 with the curve for 80° in Fig. 16.

[7] Dugald Clerk, Gaseous Expt. Com. Reports, **1912**, 23, 24.

[8] Katz, U. S. Bureau of Mines, *Technical Paper* **183**.

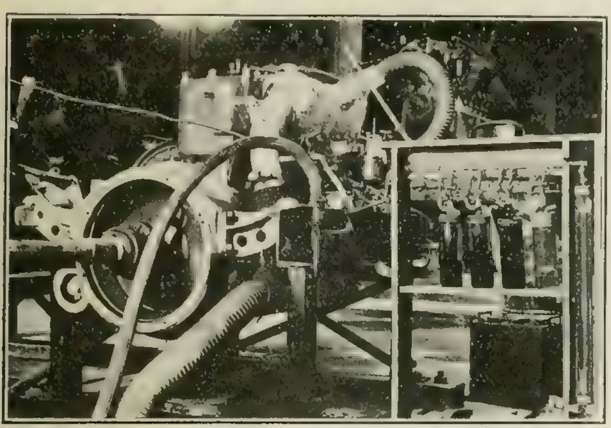

Fig. 11—Set-up for Sampling and Analyzing Exhaust Gases

Experimental Work

Fig. 9 shows the set-up used to determine the action of a gasoline engine when subject to various conditions of temperature and concentration of mixture. The engine is shown connected to a hydraulic dynamometer. Speed was taken by an indicating revolution counter, and the torque was determined by balancing the arm of the dynamometer on the platform of a Fairbank's scale. A mercury manometer was connected to the intake manifold so that the pressure in the manifold might be recorded. A quarter-inch pipe threaded and cut as shown in Fig. 8 was inserted in the exhaust pipe in the manner indicated. To this pipe a modified form of Orsat apparatus and vacuum pump used as an aspirator were connected as shown in Figs. 10 and 11. Using the vacuum pump in this manner kept the tubing clear of dead gas.

Fig. 12 shows the construction of the pipets used in the Orsat apparatus. The caustic and pyrogallate pipets were filled with glass tubes and the two cuprous chloride pipets were filled with twisted copper strips. The pipets were connected to the capillary manifold by rubber tubing provided with pinchcocks. The gas, admitted through tube A, bubbled through the solution, which was displaced and forced into the outer vessel. The gas was removed from the pipet through tube B. Five passages of the gas through the absorbing solution were found ample for all gases encountered in this work.

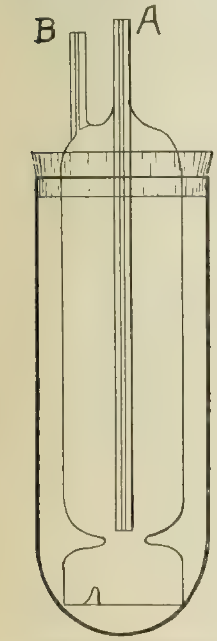

Fig. 12—Absorption Pipet

Fig. 13 is a chart used to determine the mixture proportion from exhaust gas analysis. It was prepared for use with the Standard gasoline obtained in Michigan in the fall of 1920 but is practically correct for the present market gasoline. The ordinate represents percentage composition of exhaust gas and the abscissa pounds of air to one pound of gasoline.

The large hot air stove over the exhaust manifold can be plainly noticed in Fig. 14, which also shows the carburetor and the thermometer in the air intake.

results—Fig. 16 shows graphically the data taken in determining the horsepower developed by the engine at wide open throttle and constant speed, but with varying mixture proportions and temperature of the air supply. By keeping the speed and throttle constant, the turbulence or agitation of the mixture is constant and its effect may be neglected. Then any change in power must be due to mixture proportion or temperature.

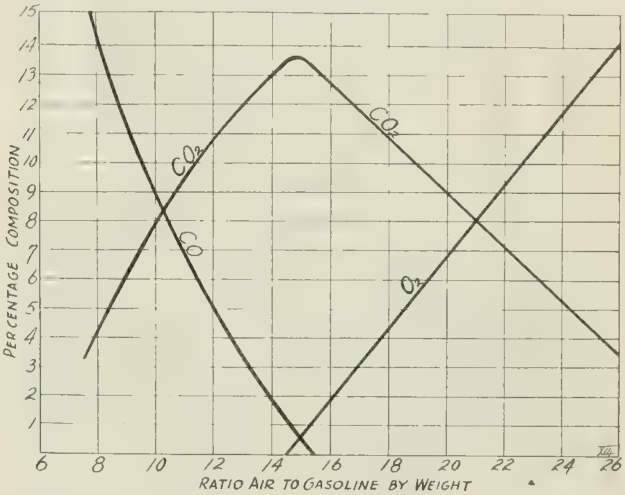

Fig. 13—Ratio Air to Gasoline from Exhaust Gas Analysis

The power and torque developed by an engine are directly proportional to the mean effective pressure of the working substance on the piston. For maximum power, it is desired to develop the maximum pressure as early as possible in the power stroke, or to explode the maximum quantity of gasoline as rapidly as possible. Maximum power is developed, particularly with cold mixtures, when the proportion of air to gasoline is slightly more than that giving maximum velocity of combustion. Increasing the temperature decreases the density of the mixture and similarly diminishes the weight of charge taken into the cylinder. Then for maximum power, a comparatively cold rich mixture is desired. With higher temperatures the velocity of reaction is greater and the power curve flattens out as the effect of mass

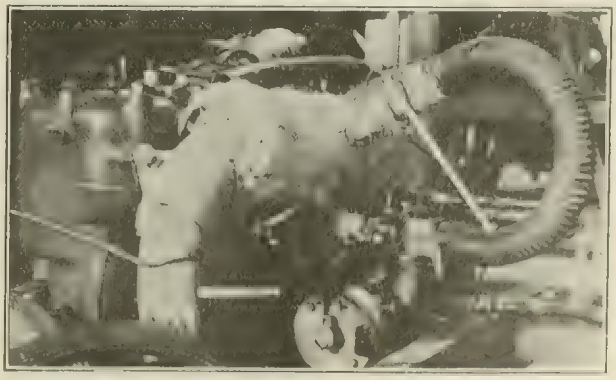

Fig 14—Carburetor Connections Showing Large Hot Air Stove and Manometer Connection in Intake Manifold

action becomes less noticeable as the influence of temperature becomes more pronounced.

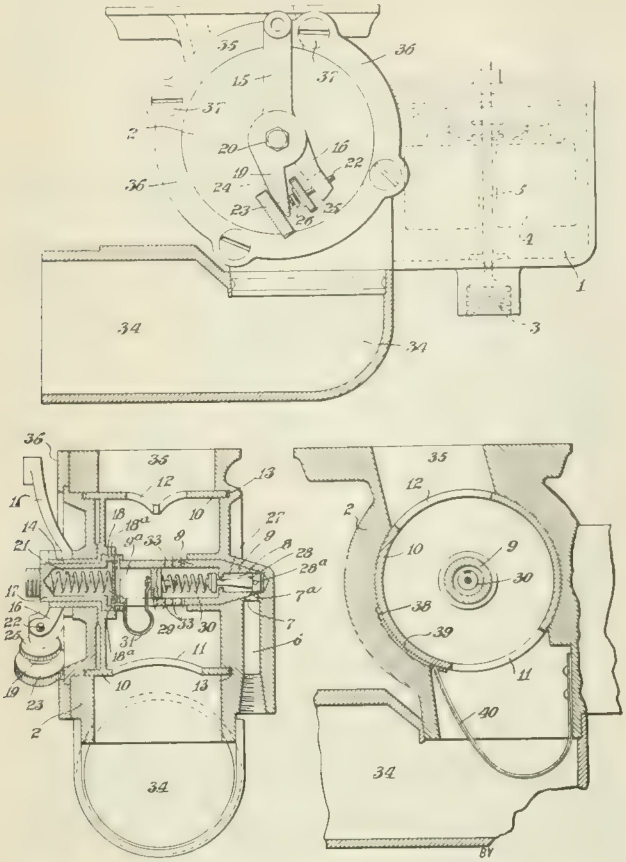

Fig. 15—Construction of Carburetor Giving Automatic Control

In all industrial combustion problems, increased efficiency can be obtained by returning as much heat as possible from the waste gases to the combustion zone by preheating the air. This is doubly true in the gasoline engine, for hot air not only helps to vaporize the gasoline but also increases the rate of combustion so that a leaner mixture can be burned with increased efficiency.

Fig. 17 shows graphically the data taken to determine the effect of mixture proportion or dilution, and temperature upon efficiency, if the throttle position is varied to maintain constant speed under constant load as is done under actual driving conditions.

With the help of these curves and a knowledge of the influence of concentration, temperature, and turbulence upon the rate of combustion, the behavior of an automobile under road conditions may be easily explained. The greatest mileage per gallon can be obtained with a hot dilute mixture, because under these conditions the engine develops its greatest efficiency. If the engine is cold, a more concentrated mixture is required to maintain the velocity of reaction above the critical point necessary for explosion. If a car being driven at constant speed along a smooth level highway, using the leanest possible mixture that can be completely burned, encounters a grade or other resistance, the engine slows down. The diminished velocity of mixture into the cylinder decreases the turbulence and velocity of combustion to such an extent that the engine backfires, misses, and may even stop, unless some measure is employed to increase the velocity of combustion. This can best be done by supplying a richer mixture until conditions have returned to the former state of normal load.

In starting a cold engine, the air has a definite weight per unit volume, which steadily decreases with increasing temperature, as shown in Fig. 19. Also the gasoline has a certain viscosity which steadily decreases with increasing temperature, so that the weight of gasoline flowing through a constant orifice increases with rising temperature as indicated in Fig. 18.[5] Then, as increasing temperature gives a greater weight of gasoline and a lesser weight of air when the reverse is desired for maximum efficiency, it is necessary that the carburetor compensate for temperature changes by automatically partly closing the gasoline orifice or opening the air port as the temperature of the air rises.

If we define normal load as the load on the engine when driving the car at a constant speed along a level highway, the suction in the manifold of an engine under normal load for different throttle openings varies as shown in Fig. 20, the average of a number of tests.

Automatic Chemical Control

A carburetor was built as shown in Fig. 15. The gasoline enters the float chamber 1 at 3 and passes through duct 6 up to the gasoline valve made by part 7 in the casing and part 7*a* in the stem valve 9, which is in the axis of the drum throttle 10 containing the air inlet 11 and the mixture outlet 12. The gasoline valve can be adjusted in relation to the throttle by the thumb screw 23 and locked in place by the nut 20 so that when the throttle lever 15 is moved the gasoline valve moves in unison with the throttle. The mixture outlet and air inlet are so calibrated that the suction in the mixing chamber is constant so long as the engine is running under "normal load." If the engine is running under any load greater than that "normal" for that particular throttle position, the suction in the manifold and in the mixing chamber will be less.

This variation in the manifold suction is utilized to vary the mixture proportions in the following manner: Within the valve stem 9 is an opening, 27, in which the governor 28 is free to reciprocate endwise of the valve stem 9. This gover-

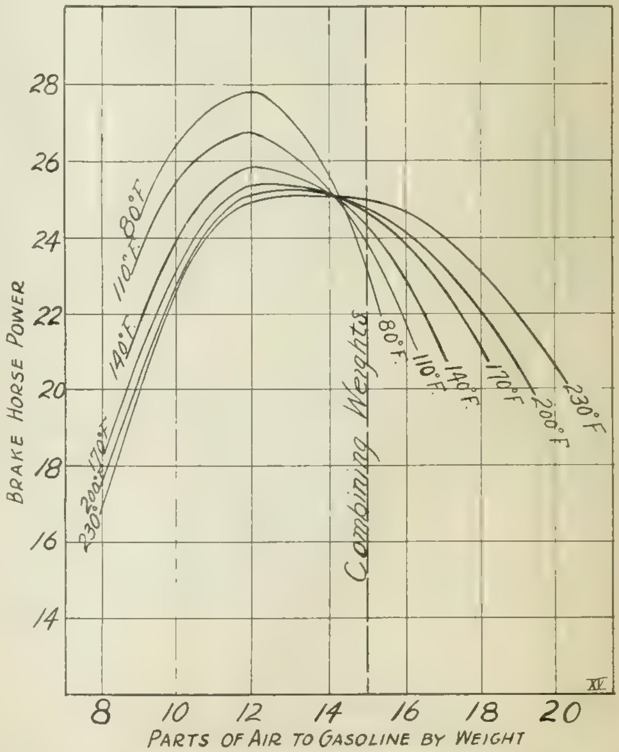

Fig. 16—Brake Horsepower Developed with Varying Temperature of Air (Figures at the End of Curves) and Mixture Concentration, with Constant Speed and Wide Open Throttle

nor 28 has a taper shank which restricts the effective area of the opening 27 by an amount corresponding to the section of the taper shank of the governor which happens to be within the opening.

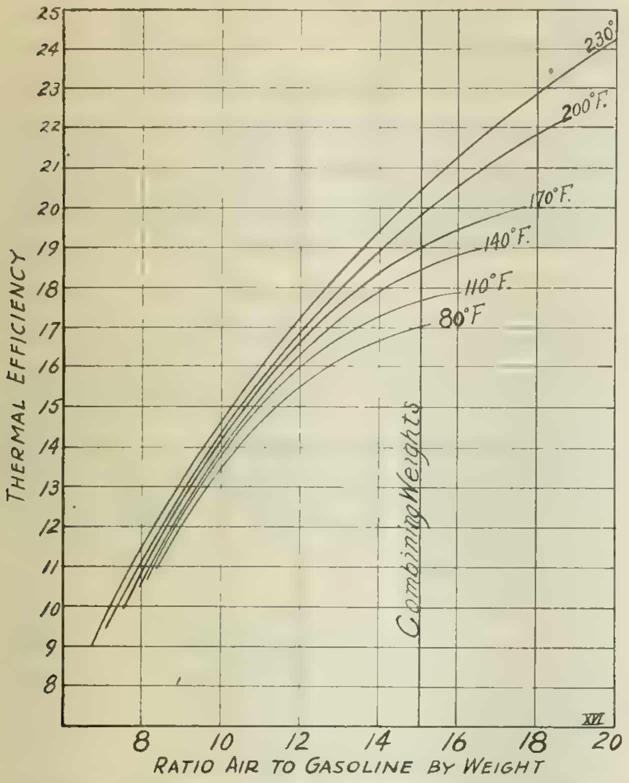

Fig. 17—Effect of Mixture Concentration and Temperatures of Air (Figures at End of Curves) upon Thermal Efficiency with Speed and Load Constant

The stronger the suction in the mixing chamber, the stronger will be the flow of fuel and the greater will be the restriction of the opening 27, as the pressure of the fuel flow upon the head of the governor compresses the spring 30, making the larger part of the taper effective and to that extent closing the fuel opening 27.

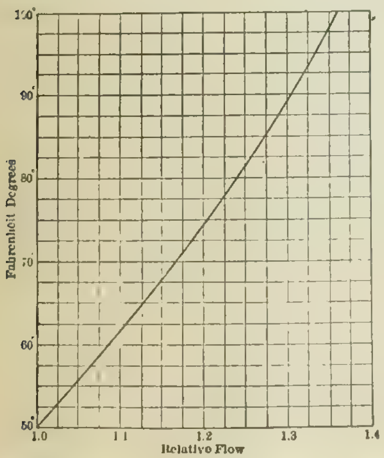

Fig. 18—Relative Flow of Gasoline through a Constant Orifice under Different Temperature Conditions

The position of the governor is also controlled by the position of the sliding block 29. The position of this block 29 is determined by the bimetal thermal regulator 31, which is fastened to the valve stem at one end and at its other end rests in a socket in block 29. Upon an increase in temperature the thermal regulator 31 curls up in a direction to move block 29 to the left and permit the governor 28 to move a like distance toward the left, thereby restricting the opening 27 an amount proportional to the movement of the thermal regulator. Upon a decrease in temperature the thermal regulator uncurls, causing the governor 28 to move a like distance toward the right, exposing a greater effective area of the opening 27.

It has been found possible to calibrate this governor and thermal regulator to obtain automatically any desired change in mixture proportion upon change in engine load or change in temperature. It is possible simply to compensate for the decreased density of air and decreased viscosity of fuel with increasing temperature, or further to restrict the flow of gasoline so as to obtain always the leanest possible or most efficient mixture. Likewise the change in mixture proportion with changing engine load may be simply sufficient to compensate for decreased turbulence to prevent missing and backfiring; or may be sufficient to change from the most economical or efficient mixture under normal conditions to the most powerful mixture when the engine is heavily loaded.

With the common type of carburetor, an expert driver using a dash adjustment and keeping the mixture as dilute or lean as temperature and load conditions will permit, can obtain much greater mileage than if he were not able so to control the mixture. But the average driver is not skilled and cannot constantly adjust the carburetor to the best advantage, even if he might care to do so. "In fact, when he has once made a carburetor adjustment rich enough to give good engine operation with a cold engine on acceleration and hill-climbing without actually causing his engine to 'gallop' under ordinary conditions, he much prefers to leave it strictly alone, using anywhere from 10 to 50 per cent more gasoline than is really necessary."[9]

The carburetor described above is designed on an exact mathematical basis to deliver a definite mixture of gasoline and air for each condition of temperature and load, and as it is automatic and positive in action much better chemical control can be obtained by its use than with a dash adjustment even in the hands of a skilled operator.

RESULTS OF CHEMICAL CONTROL—By application of the principles of chemical control developed above, and the means for positively and automatically obtaining that control as described, the miles per gallon have been invariably increased from 25 to over 100 per cent over that previously obtained.

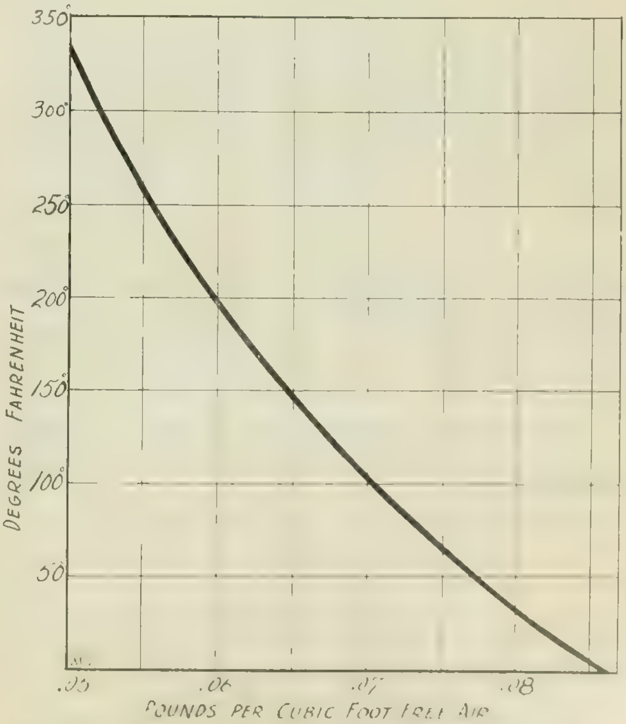

Fig. 19—Density of Air at Different Temperatures

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[9] W. E. Lay, "Saving Fuel with the Carburetor," J. Soc. Automotive Eng., 7 (1920), 188.

A standard Ford touring car being driven without dash adjustment averaged 19 mi. per gal. By utilizing the dash adjustment the same driver was able to increase this figure to 23 mi. per gal. Applying automatic chemical control to the same standard car, the same driver maintained a monthly average of over 30 mi. per gal. and on one day of cross-country driving ran 36 mi. per gal.

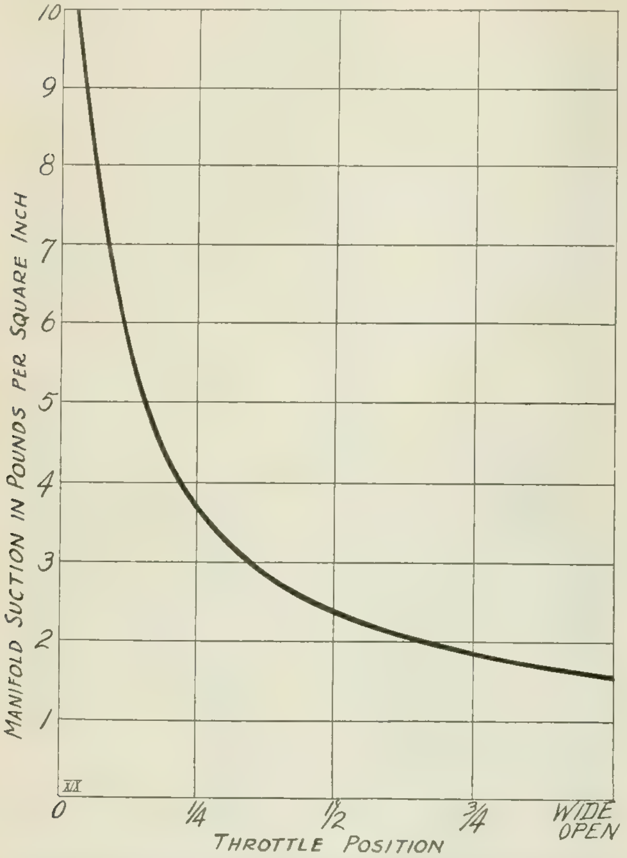

Fig. 20—Manifold Suction for Different Throttle Positions with Engine under "Normal Load"

In similar tests on a Pope-Hartford Six weighing 4400 lbs., automatic chemical control increased the mileage from 8 to 18 mi. per gal.

SUMMARY

The combustion or explosion of a gasoline-air mixture is essentially a complex chemical reaction and as such is susceptible to chemical control.

The most important consideration is the velocity of reaction, which is determined by concentration, turbulence, and temperature as follows:

1—The mixture of maximum reaction velocity has always an excess of combustible over the combining proportions and the wider the variation from this ratio, the lower the reaction velocity.

2—Turbulence increases the reaction velocity.

3—As the temperature is raised, the velocity of reaction is increased.

As the greatest efficiency is obtained with the most dilute mixture that can be burned under existing conditions, it follows that the greatest mileage can be obtained with dilute, hot mixtures with a high degree of turbulence.

As the temperature decreases the mixture must be made more concentrated to maintain the velocity of reaction.

Since the turbulence decreases as the engine speed decreases, the reaction velocity must be maintained by increasing the concentration of the mixture as greater load is put on the engine.

Means for automatically obtaining the proper chemical control are described and the results of such control are briefly outlined.

ACKNOWLEDGMENT

The writer wishes to acknowledge the assistance of a number of students, particularly Mr. A. A. Young and Mr. E. A. Goodman, in making the tests described above, and the kindness of Prof. W. E. Lay in extending privileges in the automotive testing laboratory.

Statistics on the Production of Fixed Nitrogen

According to the final report of the Department of Scientific and Industrial Research, of Great Britain, no definite conclusions are possible as to the post-war demand for fixed nitrogen, especially that required for fertilizing purposes. The prospects indicate that although the potential output has been greatly increased by the provision of large fixation plants during the war period, yet the total demand for fixed nitrogen is growing at an even greater rate. The actual output of fixed nitrogen for 1912 and the approximate maximum potential supply for 1920 in long tons is as follows:

	1912 Output of Product	1920 Productive Capacity
Chile nitrate industry (assumed 95 per cent product)	2,586,975	2,966,061
By-product industry (sulfate assumed 24.5 per cent ammonia)	1,229,773	2,015,440
Fixation industry—cyanamide (assumed 16 per cent nitrogen)	126,538	1,777,000
Nitrate of lime and arc process products (assumed 13 per cent nitrogen)	75,000	290,400
Synthetic ammonia	......	1,503,000
Total of fixation industry	201,538	3,570,400
GRAND TOTAL	4,018,286	8,551,901

Since the price of Chile nitrate may be said still to dominate that of fixed nitrogen generally, the statistics relating to it are of great importance and are presented in fairly complete form.

PRODUCTION AND PRICES OF CHILEAN NITRATE

	Production long tons	Price long ton ex ship Liverpool	Price long ton f. o. b. Chile
1913	2,464,540	£11 1 8	.....
1914	2,432,328	10 8 9	£8.56
1915	1,734,932	12 13 0	6.99
1916	2,877,899	17 12 5	8.45
1917	2,966,061	25 5 0	10.0
1918	2,831,026	26 6 6	13.12
1919	1,658,826	21 2 9	13.3
1920 (first half)	1,182,000	24 18 8	17.5
(second half)	1,310,000	23 17 0	.....

NITROGEN FIXATION PLANTS

	Plants	Capacity Metric Tons
ARC PROCESS		
Germany	2	4,000
France	2	1,300
Norway and Sweden	3	30,000
Italy	2	1,200
Canada	1	800
United States	1	300
Switzerland	1	700
TOTAL	12	38,300
CYANAMIDE PROCESS		
Germany	7	120,000
Austria	2	22,000
France	9	58,000
Norway and Sweden	3	28,000
Italy	5	18,000
Switzerland	3	7,000
Canada	1	12,000
Japan	4	20,000
United States	1	40,000
TOTAL	35	325,000
SYNTHETIC AMMONIA PROCESS		
Germany	2	300,000
United States	1	8,000
TOTAL	3	308,000
GRAND TOTAL	50	671,300

Heat Transfer[1,2,3]

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All chemical reactions are accompanied by the absorption or evolution of heat; hence in every problem in chemical engineering design, provision must be made for the satisfactory transference of the heat quantities. Furthermore, even in processes which involve practically no chemical changes, one or more problems of heat transfer usually arise.

It is well understood that heat may flow by three mechanisms, which may be defined[1,*] as follows:

> **Conduction**—Heat passing from one part of a body to another part of the same body, or from one body to another in physical contact with it, without appreciable displacement of the particles of the body, is said to flow by conduction.
>
> **Convection**—Convection is the transfer of heat from one place to another within a fluid (gas or liquid) by the mixing of one portion of the fluid with another.
>
> **Radiation**—A hot body gives off heat in the form of radiant energy. When this energy strikes another body, part is reflected. If this second body is transparent or translucent, another part is transmitted. The remainder is absorbed, and quantitatively transformed into heat.†

In all cases of commercial importance the heat flows by at least two of these mechanisms. The laws governing the flow by the various mechanisms have long been available and the mathematical statements of these laws have been verified by numerous experiments. The all-important problem is not a further elucidation of these laws, but the development of equations from which the numerical values of the *coefficients* of heat transfer may be calculated. Such equations may be used both in designing new apparatus and, for apparatus already built, in predicting the change in capacity caused by changing operating conditions.

Object of Present Articles

It is the purpose of this series of articles to review the reliable data for these coefficients, to present new data for certain important cases for which sufficient data are not available, and, where possible, to correlate these data by developing general formulas for certain cases.

Where heat flows by radiation, it usually flows also by the mechanisms of conduction and convection acting simultaneously. Since the law governing the flow by radiation is quite different from that governing the flow by conduction and convection, the rate of flow by radiation is calculated by the proper equation and added to that calculated for the flow by the other two processes. The cases in which the flow by conduction and convection is the controlling factor will be discussed first, but before taking up definite cases it is desirable to discuss in detail the mechanism of flow by conduction and convection, and the method of analyzing such data.

Potential Concept

The flow of heat by conduction and convection is determined by Newton's law in the following form,[2] which is analogous to Ohm's law for the flow of electricity:

$$\frac{Q}{\theta} = \frac{\Delta T}{r_1 + r_2 + r_3} = \frac{\Delta t_1}{r_1} = \frac{\Delta t_2}{r_2} = \frac{\Delta t_3}{r_3} \qquad (1)$$

where $\frac{Q}{\theta}$ = B. t. u. transferred per hr.

ΔT = Average *over-all* difference in temperature between the hot and cold fluids.

Δt = Average difference in temperature between two boundaries of any definite part of the path.

r = Thermal resistance of any definite part of the path.

Since three resistances are met in the cases which are to be discussed later, these are indicated by the subscripts 1, 2 and 3.

Film Concept[1]

When a liquid or gas is in contact with a solid there is strong evidence to show the presence of an adhering relatively stationary film[3] of fluid on the surface of the solid, a film which becomes thinner as the velocity of the fluid parallel to the surface increases, but which breaks away from the solid only at very high velocities, if at all. Through such a film, heat can be transmitted by conduction only, although once the heat has penetrated through the film the hot molecules are picked up and carried away mechanically by the swirling motion of the main body of the fluid, *i. e.*, the transfer is mainly a matter of convection, and in the latter case the resistance to flow will be negligible. Since most liquids and gases are exceedingly poor conductors of heat, it is not surprising to find a large resistance to heat flow at the boundary surface of a fluid and solid (and also at the boundary between a liquid and a gas), accompanied by a large drop in temperature at this point. The temperature change in the neighborhood of a solid-fluid boundary is indicated in Fig. 1. Through the solid there is a fall, t_2–t_3, which is usually small compared to the temperature drop in the boundary itself. Through the surface film the drop t_3–t_4 is very great, but once the zone of stationary fluid is passed the temperature soon reaches that of the main portion of the fluid. No attempt has been made to draw Fig. 1 to scale.

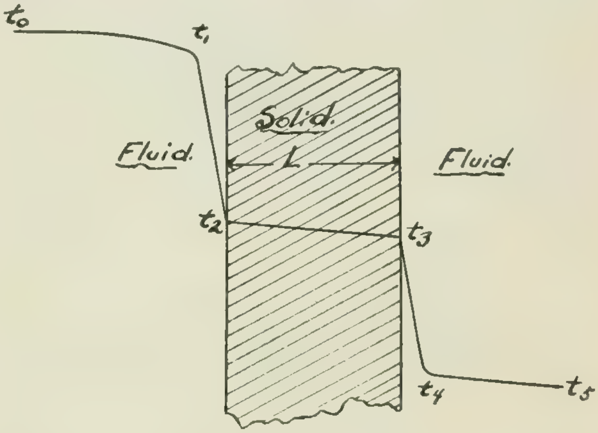

Fig. 1

The rate of heat loss by conduction through a layer of any material of thickness L and conductivity k may be calculated from the following equation:

$$\frac{Q}{\theta} = \frac{k}{L} (A) (t_3 - t_4) \qquad (2)$$

where t_3 and t_4 = temperatures of the two faces of the layer.

k (or K) = thermal conductivity of the material, expressed as B. t. u. per hr. per sq. ft. per ° F. per ft. thickness.

This equation may be applied to flow of heat through the stationary film of fluid on the surface of solid, provided the term h be used to designate the ratio k/L, where L is a defi-

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[1] Received November 5, 1921.

[2] Published as Contribution No. 4 from the Department of Chemical Engineering, Massachusetts Institute of Technology.

[3] Part I of series of articles on this subject.

[*] Numbers in the text refer to Bibliography, page 18.

† Except in those relatively rare cases where photochemical reactions are induced, or energy is consumed in other special ways.

nite (though unknown) effective thickness of the surface film; *i. e.*, Equation 2 becomes:

$$\frac{Q}{\theta} = hA\,(t_3 - t_4) \qquad (3)$$

This coefficient h is often called the "film coefficient" or "surface coefficient." In English units, h is expressed as B. t. u. per hr. per sq. ft. per ° F. temperature difference. In contradistinction to k, the "coefficient of conductivity" previously discussed, *the "surface coefficient" (h) contains no element of thickness.*

Thus it is seen that in the many important cases where heat is flowing from one fluid through a retaining wall to another fluid, three resistances are met. The resistance (r_1) met by the heat in flowing from the hotter of the two fluids to the retaining wall is known to be proportional *directly* to the effective thickness (L_1) of the surface film of fluid at this boundary and *inversely* as the product of the specific thermal conductivity (k_1) of the first fluid film and the surface area (A_1) of that boundary. The thermal resistance (r_2) of the retaining wall is known to be proportional *directly* to the actual thickness (L_2) of the retaining wall and *inversely* as the product of the specific thermal conductivity (k_2) of the retaining wall and the mean area (A_2) of the retaining wall. The thermal resistance (r_3) from the retaining wall to the colder of the two fluids is known to be proportional *directly* to the effective thickness (L_3) of the surface film between the retaining wall and the colder fluid and *inversely* to the product of the specific thermal conductivity (k_3) of this film and its surface area (A_3). In other words,

$$r_1 = \frac{L_1}{k_1A_1} = \frac{1}{h_1A_1};\ r_2 = \frac{L_2}{k_2A_2};\ \text{and}\ r_3 = \frac{L_3}{k_3A_3} = \frac{1}{h_3A_3} \qquad (4)$$

Equation Used in Practice

In practice, instead of using Equation 1, engineers are accustomed to use Newton's law in the following familiar form:

$$\frac{Q}{\theta} = (H)\,(A)_{av.}\ (\Delta T)_{av.} \qquad (5)$$

where H = an *over-all* coefficient of heat transfer from the hotter to the colder fluid, based on a suitable area ($A_{av.}$) of heat transfer surface. (Units: H = B. t. u. per hr. per ° F. average over-all temp. diff. per sq. ft. of suitable heat transfer area.)

The use of this equation is standard practice, and no objection is raised to this procedure, *provided* the value of H is correctly determined. The problem confronting the designer is the estimation of the numerical value of this over-all coefficient, and it will be shown that it is to be determined by a large number of factors.

A comparison of the preceding equation shows:

$$HA_{av.} = \frac{1}{r_1 + r_2 + r_3} = \frac{1}{\dfrac{L_1}{k_1A_1} + \dfrac{L_2}{k_2A_2} + \dfrac{L_3}{k_3A_3}} = \frac{1}{\dfrac{1}{h_1A_1} + \dfrac{L_2}{k_2A_2} + \dfrac{1}{h_3A_3}} \qquad (6)$$

Consider the case where steam is condensing at constant pressure on the outer surface of a pipe and cooling water is flowing throughout the pipe at a definite velocity. Each of the three resistances will have a definite value under these conditions, thus fixing the value of the over-all coefficient H. Now if the water velocity be doubled, the thickness of the film of water on the tube wall will be decreased. Experimentally, it is found that this thickness is not quite halved, and hence h_3 is not quite doubled; in general, the coefficient h_3 between the pipe and the cooling water varies directly as some power, n, of velocity. Now the other two resistances will remain practically unchanged, so if an attempt is made to express H as a function of the water velocity, it will result in the introduction of this variable to a power other than the true value of n. The literature furnishes numerous examples of such cases, and while the formulas proposed by such writers would give the correct result if *all* the experimental conditions were reproduced, they furnish little information to one interested in the numerical value of H for a case in which the mechanism is identical, and yet where a different combination of fluids and kinds of retaining wall is involved. Furthermore, it is true that such writers have neglected to include one or more very important variables in their equations (such as viscosity), with the result that variables shown in their equations for H must also take care of fluctuations in the variables omitted. Since viscosity varies quite rapidly with temperature, this last situation makes it practically impossible to duplicate the results of such experimenters even when working with the same fluids and retaining walls, unless one is within the same range of temperature that prevailed in the experimental work. The logical and by far the simplest method is the development and tabulation of equations for the various *film* coefficients. With reliable data of this sort available, the designer can calculate the film coefficients for the case of interest to him and combine them by means of Equation 6, using the resulting value of $HA_{av.}$ in Equation 5. When it is realized that nine or more variables affect the over-all coefficient H in the important case of the transfer of heat in condensers, it is seen that it is practically hopeless to get an accurate expression for H, unless one adopts the simplification of calculating the special value of H for the particular case in hand from equations involving h_1 and h_3, each of which is determined by a number of variables fewer than those which determine H. The truth of this statement will be illustrated by the use of equations given below. It is felt that the lack of progress in the development of equations for the prediction of heat transfer coefficients is due primarily to the prevailing custom of submitting the data in the form of *over-all* coefficients (H), and the failure to utilize suitable "mental pictures" concerning the various resistances involved.

Cases to Be Considered

The study of the film coefficients of heat transfer, h, by the joint mechanism of conduction and convection will include the following:

I—Condensing vapor to solid (h_v).
II—Liquid (not boiling) to solid, or vice versa (h_L).
III—Gas to solid, or vice versa (h_g).
IV—Solid to boiling liquid (h_b).

I—CONDENSING VAPOR TO SOLID

Previous Work and Scope of Present Investigation

In spite of the numerous tests of heat transfer apparatus heated by condensing vapors, the only reference found concerning direct measurements of the film coefficient (h_v) are those by Clement and Garland[4] who investigated the film coefficient from condensing steam to the outer surface of a 1-in. steel tube. The direct measurement of this coefficient was made possible by the use of thermocouples flush with the outer tube surface. The values of h_v observed by these investigators ranged from 1470 to 2410 B. t. u. per hr. per ° F. difference in temperature between steam and pipe surface per sq. ft. film area. These observers seem to have made no attempt to explain these variations or to suggest values for vapors other than steam.

Because of the lack of data in this important field, the writers have undertaken an investigation to obtain data for a number of condensing vapors, for the ultimate purpose of developing a general formula from which the coefficent from any condensing vapor to a pipe could be predicted.

VARIABLES INVOLVED

Remembering that the film coefficient of heat transfer, h_v, in question is determined by the ratio of the thermal conductivity, k, of the condensate to the effective thickness, L, of the condensate on the tube, the authors predicted that h_v would be affected directly by the thermal conductivity[5] of the condensate, and inversely by the viscosity[6] of condensate, because the more viscous the condensate, the greater would be the thickness of the layer of condensate adhering to the tube. If the surface of the tube is coated with rust or other foreign material to produce an appreciable temperature drop a "cleanliness"[7] correction must be made, which also takes care of the surface condition or roughness of the tube. Possibly some function of velocity (either parallel or at right angles to the tube, or both) will affect the coefficient, and if this is the case a correction for hydraulic radius, m, will also have to be made, for the reason developed under Case III of this series. An additional variable of great importance is the proportion of noncondensable gas[7] present in the vapor.

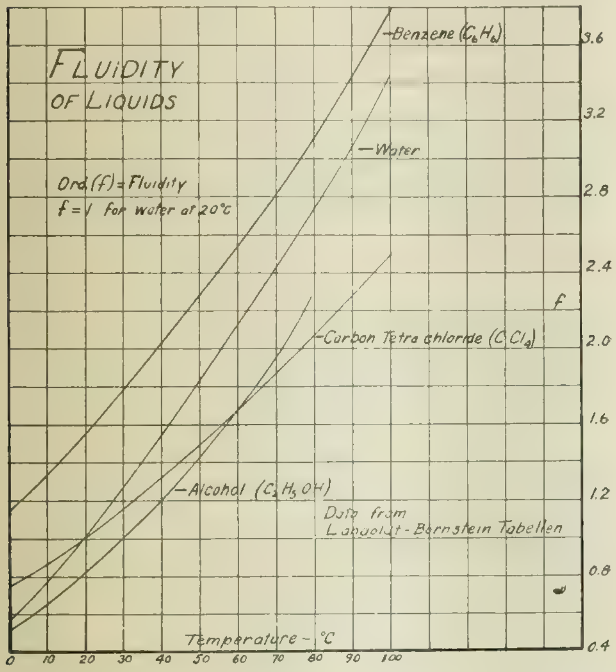

FIG. 2

Since viscosity is approximately a hyperbolic function of temperature, and fluidity (the reciprocal of viscosity) is nearly a straight line function of temperature, it was decided to introduce fluidity in the numerator of the equation for h_v instead of viscosity in the denominator.[*] The variation of fluidity f of several liquids with temperature is shown in Fig. 2.

Hence it was expected that the general formula for a vapor containing a small but uniform proportion of noncondensable gas would take the form:

$$h_v = (b)\ (c_1)\ (k)\ (f)\ (v)^n/(m)^p \qquad (7)$$

where h_v = predicted value of the film coefficient of heat transfer between a condensing vapor and a pipe, expressed as B. t. u. per hr. per sq. ft. per ° F.
b = Experimentally determined coefficient of proportionality.
c_1 = Cleanliness factor, as previously defined.
k = Thermal conductivity of condensate on the wall of the tube, B. t. u. per hr. per ° F. per sq. ft. per ft. thickness.
f = Fluidity of condensate at average film temperature in relative[†] units. See Fig. 2 for values.
v = Average velocity of vapor, parallel to the tube or at right angles to the tube, in convenient units.
n = Exponent of velocity to be experimentally determined.
m = Hydraulic radius of vapor passage, in feet.
p = Exponent of hydraulic radius, to be experimentally determined.

APPARATUS AND METHOD USED IN PRELIMINARY EXPERIMENTS

The saturated vapor being investigated was passed through the annular space between standard 1.5-in. steel pipe and a 0.675-in. o. d. and 0.49-in. i. d. brass pipe placed concentrically with the jacket. The vapor temperatures in the jacket were taken at points very close to the entrance and exit by means of calibrated mercury thermometers, and any excess vapor and the condensate from this "main" condenser were led to an auxiliary condenser. The condensate drained from the jacket by gravity due to a pitch of 1 in. per ft. of jacket. The cooling water flowed through the brass pipe parallel to the flow of vapor, thence by gravity to a tank placed on scales. The rise in temperature of cooling water was determined from the readings of two calibrated mercury thermometers, the bulbs of which were placed at the center line of the brass pipe directly under the thermometers in the vapor. The rate of heat transfer was then readily obtained by observing the weight of water passed in a definite period of time. The "skin" temperatures of the outer surface of the brass pipe (at two points directly under the thermometers in the vapor line) were measured by the use of calibrated "base-metal" thermocouples, using a millivoltmeter and a "cold junction" in the standard manner. The actual distance between each pair of couples and thermometers was 47.75 in.

TABLE I (CORRECTED DATA)

RUN No.	Temp. ° C. (Outer) Surface Brass Pipe Entrance (1)	Exit (2)	Temp. ° C. of Vapor Entrance (3)	Exit (4)	Temp. ° C. Cooling Water Entrance (5)	Exit (6)	Cooling Water Lbs./Hr. (7)
1	78.5	81.5	100.6	98.0	19.0	37.8	1585
2	78.7	79.5	101.0	98.5	19.1	34.2	2030
3	81.5	81.2	106.4	104.0	19.1	35.4	2105
4	79.2	77.6	102.0	99.0	19.5	34.7	2195
5	101.5	106.5	117.0	115.0	17.0	48.6	900
6	88.0	84.5	100.3	99.0	17.3	39.8	973
7	88.5	85.1	99.5	98.8	17.0	40.0	942
8	54.5	64.0	77.2	73.0	19.5	38.5	156
9	56.5	67.0	80.4	76.4	19.5	42.2	147
10	61.0	69.5	80.8	77.0	19.3	42.2	141

The rate of water flow was adjusted to give a sufficient rise in temperature of cooling water, and the rate of flow of vapor was adjusted to suit the capacity of the condenser. In some cases, excess vapor was used in order to determine the effect of varying the velocity of the vapor.

RESULTS

Table I shows the data[8] obtained, with all corrections for thermometer calibrations and conversions of thermocouple reading to temperatures made. The rate of flow of cooling water has been reduced to an hourly basis and all temperature readings are the average of four sets of readings taken during each run, the variation in no case exceeding 1° C.

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[*] Under certain conditions of operation the temperature of the condensate will be sufficiently different at entrance and exit of the apparatus to raise the question of the proper average viscosity of the condensate. Inasmuch as viscosity is not a linear function of temperature it will be difficult to work out a correct formula for obtaining the average viscosity. On the other hand, since fluidity is a straight line function of temperature it matters little whether one averages temperatures and reads off the corresponding fluidity or whether the fluidity corresponding to each temperature is determined and then averaged. By dealing with fluidities one obtains the correct average regardless of which method of averaging is used, whereas in working with viscosities different results would be obtained, neither of which would be correct.

[†] Viscosity data in c. g. s. units (poises, or second dynes per sq. cm.) were taken from the literature, and since the viscosity of water at the standard temperature chosen (20° C.) is 0.0100 in these units, f (the fluidity of the liquid at the temperature in question relative to water at 20° C.) = the reciprocal of the viscosity in centipoises. For example, the c. g. s. viscosity of liquid benzene at 70° C. is 0.00355, and the corresponding value of f is 1/(0.00355)(100) = 2.82 for benzene at 70° C.

Table II shows results of calculations from the observed data.

TABLE II

RUN No.	B.t.u./Hr. Transferred (1)	Average Temp. Diff. Steam to Pipe (° C.) (2)	h_v (3)	f (Cond.) (4)	K (Cond.) (5)	h_v/fk (6)	Vel. Cooling Water Ft. per Sec. (7)	h_w (Obs.) (8)	Ratio $\frac{h_w\text{ (Obs.)}}{h_w\text{(Calc.)}}$ (9)
				STEAM					
1	53,600	19.3	2190	3.05	0.329	2180	5.39	1280	1.20
2	55,200	20.6	2110	3.05	0.329	2100	6.90	1300	1.06
3	61,700	23.7	2060	3.12	0.329	2010	7.16	1420	1.10
4	60,000	22.1	2150	3.04	0.329	2150	7.45	1460	1.10
5	51,200	12.0	3360	3.86	0.329	2650	3.06	851	1.12
6	39,400	13.4	2310	3.16	0.329	2220	3.31	805	1.09
7	39,000	12.4	2475	3.16	0.329	2380	3.20	789	1.10
				CARBON TETRACHLORIDE VAPOR					
8	5,340	14.8	283	1.85	0.0610	2510	0.533	196	1.05
				BENZENE VAPOR					
9	6,010	15.5	306	2.81	0.0806	1350	0.50	217	1.18
10	5,820	12.6	366	2.87	0.0806	1580	0.48	187	1.06
								Av.	1.11

SAMPLE CALCULATIONS (DATA FOR RUN 1, STEAM)

(a) *Calculation of h_v*

$\frac{Q}{\theta}$ = (1585) (1.8) (37.8 − 19.0) = 53,600 B. t. u. per hr. (Col. 1, Table II).

Temperature diff. (° C.) initial = 100.6 − 78.5 = 22.1
Final = 98.0 − 81.5 = 16.5

$$\text{Mean} = \frac{22.1 + 16.5}{2} = 19.3 \text{ (Col. 2, Table II).}$$

$$\text{Condensing surface} = \frac{(47.75)\ (0.675)\ (3.14)}{144} = 0.703 \text{ sq. ft.}$$

Observed film coefficient on vapor side (h_v) =

$\frac{53{,}600}{(19.3)\ (1.8)\ (0.703)}$ = 2190 B. t. u. per hr. per ° F. per sq. ft. (Col. 3, Table II).

$$\text{Temp. condensate} = \frac{100.6 + 98.0 - 19.3}{2} = 89.6 \text{ (°C.).}$$

Corresponding fluidity (see Fig. 2) = 3.05 (Col. 4, Table II).

Thermal conductivity (K) of condensate = value in Landolt-Börnstein's "Tabellen" at room temperature converted into English units (B. t. u. per hr. per sq. ft. per ° F. per ft.) by multiplying by 242 (Col. 5, Table II)

$$\frac{h_v}{f\text{K}} = \frac{2190}{(3.05)\ (0.329)} = 2180 \text{ (Col. 6, Table II).}$$

(b) *Calculation of hw (observed)*

To calculate the film coefficient on the water side, it is necessary to know the drop in temperature from the inner wall of the brass tube to the main body of the water in the tube. This equals the drop from the outer wall of the brass tube to the water, less the drop through the brass tube. The latter is readily calculated, since the thermal conductivity and thickness of the brass tube is known, namely, k = 63.0 B. t. u. per hr. per sq. ft. per ° F. per ft., and L = (0.675 − 0.49)/(2) (12) or 0.00771 ft.

The average area of the tube (based on the mean diameter of 0.583 in.) is (47.75) (0.583) (3.14)/144 = 0.607 sq. ft., and the resistance (L/KA) is (0.00771)/(63.0) (0.607) = 0.000202.

The ° C. drop through the brass tube is:

$$\frac{Q\ (0.000202)}{\theta\ (1.8)} = \frac{Q/\theta}{8910}$$

The drop for Run 1 is, then, 53,600/8910 = 6.0° C.

From outer wall to water (° C.) =

Initial = 78.5 − 19.0 = 59.5
Final = 81.5 − 37.8 = 43.7

$$\text{Mean} = \frac{59.5 + 43.7}{2} = 51.6.$$

From inner wall to water = 51.6 − 6.0 = 45.6° C.

$$\text{Inside cooling surface} = \frac{(47.75)\ (0.49)\ (3.14)}{144} = 0.510 \text{ sq. ft.}$$

Observed coefficient, pipe to water, $hw = \frac{53{,}600}{(0.510)\ (1.8)\ (45.6)}$ = 1280 B. t. u. per hr. per ° F. per sq. ft. (Col. 8, Table II).

(c) *Predicted value film coefficient (hw)*

As shown under Case II of this series,

$hw = (340)\ (c_1)\ (\text{K})\ (f)\ (u^{0.76})\ (\text{S}^{0.17})$, where S = reciprocal of hydraulic radius in feet.

K = 0.329, as before.

$$\text{S} = \text{shape factor} = \frac{48}{0.49} = 98;\ \text{S}^{0.17} = 2.18.$$

$$hw = (340)\ (0.329)\ (c_1)\ (f)\ (u)^{0.76}\ (2.18) = 244\ (c_1)\ (f)\ (u^{0.76}).$$

In order to make a comparison, call cleanliness coefficient (c_1) = 1.00.

$$u = \frac{\text{(lbs. cooling water per hr.)}}{(62.3)\ \text{(cross-sectional area of tube, sq. ft.)}\ (3600)} = \text{average}$$

$$\text{water velocity in feet per second} = \frac{\text{(lbs. water per hr.)}}{(62.3)\ \frac{(0.49)\ (0.49)}{144}\ (0.785)\ (3600)} = \frac{\text{lbs. cool. water per hr.}}{294}.$$

For Run 1, u = 1,585/294 = 5.39 ft. per sec. (Col. 7, Table II).

Average temp. of water $= \frac{19.0 + 37.8}{2}$ = 28.4° C., and corresponding fluidity, f (from Fig. 2), is 1.22.

Whence h_w (predicted) = (244) (1.0) (1.22) $(5.39)^{0.76}$ = 1070 B. t. u. per hr. per sq. ft. per ° F.

Ratio of h_w (observed to calculated) = 1280/1070 = 1.20 (Col. 9, Table II).

DISCUSSION OF RESULTS

As shown by the first seven runs in Column 3, Table II, the average of the observed coefficient of heat transfer from condensing steam to pipe is about 2400 B. t. u. per hr. per ° F. per sq. ft., which checks fairly well with Clement and Garland's range of 1470 to 2410. Of course there is no reason to believe that the percentage of air in the steam was exactly the same in the two series. The observed coefficient from condensing vapor to pipe in the case of carbon tetrachloride and benzene (see Runs 8, 9, and 10, Col. 3, Table II) are approximately 280 and 340, respectively. Thus it is seen that the coefficient (h_v) in the case of steam is approximately eight times that observed for these two organic vapors.

If each individual value for the vapor film coefficient is divided by the conductivity and fluidity of the condensate, the average is 2240 for the steam runs, 2500 for the carbon tetrachloride, and about 1500 for the benzene (see Col. 6, Table II). Thus by correcting for fluidity and conductivity of the condensate, the eight-fold ratio between organic vapor and steam is reduced to less than two-fold. It will be noted that no allowance was made for variation of thermal conductivity of condensate with temperature, as no reliable data were available for this purpose. The values used for K in English units were obtained by multiplying those quoted for room temperature in the 1912 Landolt-Börnstein Tables by the conversion factor of 242, which converts thermal conductivity from c. g. s. (French) to English units.

It must be remembered that the ratio of h to fk should be further corrected for variations in concentration of noncondensable gas in the vapor and vapor velocity. No attempt was made in these preliminary experiments to control the percentage of noncondensable gas, which may have been present to the extent of the solubility of air in the liquids vaporized. In some of the runs excess vapor was used, and it appears that h/fk varies somewhat with vapor velocity. However, the few points available at present do not warrant the introduction of a velocity correction at this time. This work is being continued and it is hoped to publish additional data at an early date.

The experimental method used also made it possible to determine directly the film coefficient of heat transfer between the brass pipe and the cooling water, and the observed coefficients on the water side, h_w, are tabulated in Column 8, Table II. By means of an equation to be quoted in the next paper of this series, the value of this water film coefficient was predicted for each of these cases and the ratio of the observed to the predicted value is tabulated in Column 9, Table II. It will be seen that the maximum fluctuation is between 1.05 and 1.20, with an "average deviation" of 3.4 per cent from the average of the ten runs (1.11), and with a "probable deviation" of 1 per cent. It is felt that these "checks" are all that could be desired, and that they show that the coefficients, h_v, on the vapor side are reliable.

THERMAL CONDUCTIVITIES OF LIQUIDS

It has been shown above that the coefficient of heat transfer between a condensing vapor and a pipe is directly proportional to the thermal conductivity of the condensate, k, in English units. Where experimental data are not available, it is desirable to have a method of predicting the thermal conductivity of the liquid in question, because the experimental determination of the liquid conductivity is a difficult matter.

In 1885 H. F. Weber[9] derived an empirical relationship between liquid conductivity, k, specific heat, c, and specific gravity, s, and found that the conductivity was approximately proportional to the product of the other two factors. While this rule worked satisfactorily for certain liquids, it was found to deviate widely in the case of others, and in 1893 Weber[10] introduced an additional correction term which satisfactorily correlated the experimental values of thermal conductivities, as shown by Table III.

TABLE III—THERMAL CONDUCTIVITY OF LIQUID[1]

SUBSTANCE	Observer	Thermal Conductivity Eng. Units K	Sp. Gr. s	Sp. Ht. c	Mol. Wt. M	$\sqrt[3]{\frac{M}{s}}$	$\frac{K}{sc}=a_1$	$\frac{K}{sc}\times\sqrt[3]{\frac{M}{s}}=a_2$
Methanol	Weber	0.12	0.81	0.586	32	3.41	0.263	0.895
Ethyl alcohol	Weber	0.1025	0.804	0.579	46	3.86	0.221	0.853
Propyl alcohol	Weber	0.0902	0.819	0.518	60	4.18	0.213	0.891
Chlorobenzene	Weber	0.0731	1.111	0.352	112.5	4.65	0.187	0.871
Carbon tetrachloride	Weber	0.0610	1.63	0.205	153.8	4.56	0.182	0.840
Benzene	Weber	0.0806	0.873	0.460	78.0	4.48	0.201	0.900
Aniline	Weber	0.0990	1.039	0.497	93	4.47	0.192	0.857
Toluene	Weber	0.0742	0.884	0.440	92	4.71	0.191	0.896
Carbon disulfide	Graetz	0.0647	1.263	0.240	76.1	3.93	0.215	0.840
Chloroform	Weber	0.0697	1.503	0.234	119.4	4.31	0.198	0.855
Water	Weber	0.329	1.000	1.006	18	2.62	0.329	0.861
Glycerol	Weber	0.155	1.26	0.576	92	4.18	0.214	0.893
Acetic acid	Weber	0.1141	1.069	0.487	60	3.83	0.220	0.842
					Av.		0.217	0.868

[1] All data are for room temperature; source Landolt-Börnstein "Tabellen," 1912 Ed.

Column 7, Table III, shows k divided by (s) (c), and it is seen that the proportionality constant a_1 in the expression

$$k = a_1 cs \tag{9}$$

varies from 0.18 to 0.33. When the values in this column are multiplied by the cube root of the ratio of the molecular weight of liquid to the specific gravity of liquid, $\sqrt[3]{\frac{M}{s}}$, the variations in the revised constant, a_2, are much less, being only from 0.84 to 0.90. Hence, Weber's revised equation states that

$$k = 0.868\ (c)\ (s)\ \sqrt[3]{\frac{s}{M}}. \tag{10}$$

Thus by Equation 10 the predicted value of k for water (in English units) is (0.868) (1) $(1)/\sqrt[3]{18}$, or 0.332, which checks well with the experimental value for water of 0.329 B. t. u. per hr. per sq. ft. per ° F. per ft. of thickness. Equation 10 indicates a variation of k with temperature. If the specific heat, c, rises more rapidly with increasing temperature than the specific gravity, s, decreases, the thermal conductivity, K, of the liquid will increase, while if the reverse is true, k will decrease. Now the effect of temperature on k has not been checked experimentally, but it is seen that the variations of c and s with temperature are in opposite directions, and hence the effect of temperature on K will not be great.

NOMENCLATURE TABLE

A = Area of heat transfer surface in sq. ft.
a_1 = "Constant" in Equation 9.
a_2 = Proportionality constant in Equation 10.
b = Experimentally determined coefficient of proportionality in Equation 7.
c = Specific heat of the condensate, B. t. u. per lb. per ° F.
ı = Cleanliness factor in Equation 7.
= Fluidity of condensate at temperature in question relative to that of water at 20° C. (68° F.) as unity. See Fig. 2 for values.
H = *Over-all* coefficient of heat transfer from hot fluid to colder fluid expressed as B. t. u. per hr. per sq. ft. per ° F. *over-all* temperature difference. See Equation 5.
h = *Film* coefficient of heat transfer in B. t. u. per hr. per sq. ft. film area per ° F. temperature drop through the *film*.
h_v = Value of h from condensing vapor to pipe.
h_w = Value of h from pipe to cooling water.
k (or K) = thermal conductivity of substance as B. t. u. per hr. per sq. ft. per ° F. drop in temperature through the substance per ft. of thickness. See Table III or Equation 10 for values of k for condensate.
L = Effective thickness of film in ft., or thickness of retaining wall in ft.
M = Molecular weight of condensate (see Equation 10).
m = Hydraulic radius in ft. = cross-sectional area (sq. ft.) of path of fluid divided by wetted perimeter in ft. For a circular pipe, m equals one-fourth the inside pipe diameter in ft.
n = Exponent of velocity, to be experimentally determined.
p = Exponent of hydraulic radius, to be experimentally determined.
Q/Θ = B. t. u. transferred per hr.
r = Thermal resistance of any definite part of the path = L/kA. See Equation 4.
s = Sp. gr. of condensate.
(ΔT) = Average *over-all* difference in temperature between hot and cold fluids (see Equation 5).
(Δt) = Average drop in temperature through any definite part of the path.
u = Average linear velocity of cooling water in ft. per sec.
v = Velocity of vapor in convenient units.

SUMMARY

1—The nature of the problems arising in the field of heat transfer has been outlined, together with a rational method for studying these problems.

2—A discussion is given of the nature of the variables likely to affect the coefficient of heat transfer in the important case of the flow of heat from condensing vapors to a pipe, and it is shown that the main variables are fluidity and thermal conductivity of the condensate and concentration of noncondensable gas in the vapors.

3—The results of preliminary experiments made to determine the numerical value of the coefficient of heat transfer between certain condensing vapors and a pipe show that the coefficient in the case of steam averages about 2400 B. t. u. per hr. per sq. ft. per ° F. and 310 B. t. u. per hr. per sq. ft. per ° F. in the case of benzene or carbon tetrachloride. It is seen that the coefficient for steam is approximately eight times that found in the case of benzene or carbon tetrachloride.

4—If this coefficient is divided in each case by the product of the thermal conductivity of the condensate and the fluidity, the resulting values for these three vapors vary less than two-fold.

5—Inasmuch as thermal conductivity plays such an important part in determining the coefficient for any given vapor, H. F. Weber's equation for predicting the thermal conductivity is quoted and its application is illustrated by a table of values.

6—These experiments are being continued for the purpose of determining the effect of other variables which may affect the coefficient of heat transfer between condensing vapor and pipe.

7—From the results of these preliminary experiments the numerical value of the coefficient of heat transfer between (0.49 in. inside diameter) pipe and cooling water is found to vary from 200 to 1500 B. t. u. per hr. per sq. ft. per ° F., while the water velocity varies from 0.5 to 7.5 ft. per sec. It is shown that these results check within 10 per cent of the values figured from an equation to be published in the next article of this series.

Acknowledgment

The writers wish to express their appreciation of suggestions offered by various friends, and of the work of Mr. A. Wishnew, who performed the greater part of the experimental work herein described.

Bibliography

1—Walker, Lewis and McAdams, "Chemical Engineering Notes."

2—(*a*) Carl Hering, *Chem. Met. Eng.*, **9** (1911), 652; (*b*) J. W. Richards, "Metallurgical Calculations," McGraw-Hill Book Co., Inc., **1918**; (*c*) See Note 1; (*d*) Marks' "Mechanical Engineering Handbook," McGraw-Hill Book Co., Inc., **1916**.

3—The existence of a stationary liquid or gas film at the point of contact with solid surfaces and its low heat conductivity has long been appreciated. The first mention of a water film was made by Peclet in 1844 ("Traite de la Chaleur-Liege," Chapter 8, p. 131) and since that date many investigators have checked this idea and demonstrated the existence of the film. The most tangible conception of the gas film is represented by Langmuir (*Phys. Rev.*, **34** (1912), 421) although the film concept was not his originally. The explanation in terms of the film concept of the effect of velocity upon heat transfer is definitely stated and the part played by velocity in tearing down this film noted.

4—Clement and Garland, Univ. of Ill., Engineering Experiment Station, *Bulletin* **40** (1909).

5—Nusselt (*Z. Ver. deut. Ing.*, **1908**, 1750) introduced the thermal conductivity of air in his formula for the film coefficient between a gas and a tube.

6—Bell (*Proc. Eng. Soc. W. Pa.*, **32** (1916–17), 797) points out that the *over-all* coefficient of heat transfer in a condenser would be a function of the fluidity of the condensate.

7—Orrok (*Trans. Am. Soc. Mech. Eng.*, **32**) introduces a cleanliness coefficient in connection with the *over-all* coefficient in a condenser, and a correction for the percentage of noncondensable gas in the steam.

8—The greater part of these data was taken from the undergraduate thesis of Wishnew (Mass. Inst. Tech. Chemical Engineering Thesis, **1921**).

9—H. F. Weber, *Berl. akad. Ber.*, **1885**, 809, and Exners Reppert, **22** (1886), 116.

10—H. F. Weber, *Wied. Ann.*, **48** (1893), 173.

The Decolorizing Action of Bone-Black[1]

By Claude H. Hall, Jr.

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This investigation was suggested by Bancroft[2] in his list of problems in colloid chemistry. There are only three important references bearing on the phase of the subject under discussion: Bancroft[3] gives a synoptical account of charcoal before the war, chiefly from an industrial point of view; Knecht[4] agrees with Patterson, but introduces no new evidence; and Patterson,[5] who describes at considerable length the extraction from bone-black, and the examination of a nitrogenous material to which is due the decolorizing action of the bone-black. The object of this investigation was to repeat the work of Patterson, which has never been confirmed, and to carry his researches a step further.

Experimental

The procedure finally adopted as most satisfactory is to digest about 15 g. of bone-black with 90 cc. of 15 per cent hydrochloric acid for 20 min., filter through an alundum crucible, and dry residue at about 120° C. The loss is approximately 30 per cent, chiefly mineral matter. Suspend the crucible containing the residue in a small beaker of concentrated sulfuric acid and allow it to remain on a water bath for 2 hrs. Filter through the same crucible and wash with 80 per cent sulfuric acid. The sulfuric acid extract is poured into 0.5 l. of water and the whole put aside for several hours. At the end of that time a brown precipitate will be found to have collected on the bottom of the beaker and may be filtered off through a fine filter. It is almost impossible to wash this precipitate, because it becomes colloidal as soon as the sulfuric acid is removed.

This extracted material is the active decolorizing agent of the bone-black, for a few drops of its concentrated suspension in water are equal in decolorizing action to several grams of good bone-black.

The next and most important step was to determine whether by the precipitation of this substance on wood charcoal, or other porous material, an active charcoal could be produced. The precipitation was carried out by mixing wood charcoal in the sulfuric acid suspension of the extract, adding water, and filtering. The material thus prepared was found to be about twice as active as the original bone-black, but this is easily explained by the fact that the extract from about 15 g. of bone-black was suspended on about 6 g. of wood charcoal.

Discussion

It may be concluded that the decolorizing action of bone-black is entirely due to a mixture of nitrogenous decomposition products of bone cartilage, etc., which are carried by the charcoal proper. These compounds are described by Patterson, and his results have been confirmed by the author. The compounds are insoluble in ethyl alcohol, ether, benzine, and chloroform, soluble in ammonium hydroxide, concentrated sulfuric acid, and concentrated hydrochloric acid, from the latter two of which they are precipitated by water. They have the empirical formula $C_{25}H_{20}N_4O_6$.

The real nature of these bodies and the mechanism of the reaction, however, still remain a mystery.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] This Journal, **13** (1921), 155.

[3] *J. Phys. Chem.*, **24** (1920), 201.

[4] *J. Soc. Chem. Ind.*, **28** (1909), 700.

[5] *Ibid.*, **22** (1903), 608.

School for Water Plant Operators

During the week of January 16, 1922, a course on "Wholesome Water Production" is to be given in Dallas, Texas, under the auspices of the city Health Department, with the coöperation of the Texas State Board of Health and the Texas Water Works Association. This is the fourth short course offered free of charge to water plant operators. The work is not highly technical, but will cover comprehensive and practical points in the purification of water.

Potash from Kelp. V—The Applicability of Kelpchar as a Bleaching and Purifying Agent[1,2,3]

By J. W. Turrentine and H. G. Tanner

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During the past few years there has been an awakened industrial interest in the unique adsorptive quality of charcoal. In many instances, products that are ordinarily purified by recrystallization, distillation, or chemical precipitation of the foreign substances can now be brought to an even higher degree of purity by a simple treatment with activated charcoal. The utilization of activated charcoal, or decolorizing carbon, as it is frequently termed, by the industries in large quantities awaits only the advent of a carbon of high activity that can meet the requirements of the trade. The possibilities along this line have been observed by many, as is witnessed by the large volume of patents and articles on decolorizing carbon recently published, and the many researches and tests conducted by industrial concerns. Carbonaceous matter of various sorts has been treated in many different ways in the hope of finding a carbon that would surpass all others in its purifying powers.

Carbons, both of vegetable and animal origin, have been used for sugar purification for over a century, and during this time favoritism has been constantly shifting among bone-black, vegetable carbons, and purely chemical methods of bleaching the sugar sirups. Recent improvements in vegetable charcoal have inclined sugar manufacturers again in this direction.

Through the work of Zerban[4] it was established that a good decolorizing carbon could be made from the Pacific Coast kelp, *Macrocystis pyrifera*, which is the kelp that has been made the basis of the kelp products industry of Southern California. Zerban found that a carbon could be prepared that was equal to the best vegetable charcoals on the market, and some of these carbons, according to Coates,[5] possess from fifty to seventy-five times the decolorizing value of good bone-black.

Subsequent to Zerban's tests, the manufacture of bleaching carbon as a by-product in the extraction of potash from kelp was incorporated in the plans for this experimental plant, and researches looking to its large-scale production were immediately inaugurated. Success attended these studies. Bleaching carbon is being manufactured from kelp in quantities of one thousand pounds per day at a fair cost, and has been successfully introduced under the trade name "kelpchar." Its manufacture will be described in a subsequent paper.

The Testing of Carbons

At the outset it was necessary to develop a reliable and quick method of determining the activity of the carbon in order that the various processes of manufacture could be controlled. No universal method seemingly exists whereby the decolorizing value of carbon on solutions of different types may be expressed, since the decolorization of a complex solution is influenced by a great many factors. Carbons are specific in their action. For these reasons, it is desirable to test a carbon in a manner as nearly parallel as possible to the way in which it will be applied on a large scale.

Wickenden and Hassler[6] advocated testing carbons designed for the purification of oils by causing the carbon to remove a dye dissolved in oil. The weight of carbon producing the same degree of decolorization as a unit quantity of another carbon selected as a standard gave the necessary data for judging the value of the carbon under test. The method is open to the objection that the carbon in the laboratory is made to remove an impurity different from those which it is expected to remove in the plant. The carbon may be specific to the dye and not to the coloring matter occurring in the oil. Of course, any method of control analysis which is empirical depends for its accuracy upon the closeness wherewith the method parallels the procedure to be observed in actual practice.

Zerban and Freeland suggested a method of determining the decolorizing value of a carbon as applied to cane-sugar sirups. Their original method prescribed boiling a quantity of dilute cane molasses with a unit amount of carbon under examination and comparing the filtrate colorimetrically with another filtrate prepared from the same amount of a second carbon chosen as a standard. Unless the two carbons were of equal quality, the filtrates produced would not agree either as to tint or intensity of color. This made comparison difficult, and to overcome this Zerban[7] and his collaborators recommended the use of a Hess-Ives tint photometer. Carbons were compared on the basis of the amount of color left in solution. If one carbon removed all but 20 per cent of the color and another all but 5 per cent, the latter was four times as efficient as the former.

In this laboratory a method of evaluating carbon has been devised for plant control which possesses simplicity and has given satisfaction.

PROCEDURE—A stock solution of molasses is prepared by dissolving 50 g. of cane molasses in about a liter of water. After bringing the solution to neutrality with sodium hydroxide or acetic acid as required, 3 cc. of glacial acetic acid, 15 g. of sodium acetate, and 2 cc. of formaldehyde are added.

Of this solution 80 cc. are brought to boiling with 2 g. of the carbon to be tested. The mixture is filtered while still hot, and the filtrate is matched with a set of filtrates prepared in the same manner but with different quantities of a standard carbon. The weights of the unknown and the standard carbon samples producing the same degree of decolorization are taken as representing the relative efficiencies of these carbons. For convenience, the ratio of these weights is calculated to the percentage basis, figuring the standard carbon as 100 per cent.

The standard carbon may be any carbon arbitrarily selected for the comparison. The set of standard filtrates deteriorates on standing, and should be prepared fresh daily.

DISCUSSION—This method combines reliability with speed. The presence of sodium acetate does not appreciably affect the action of the carbon on the natural impurities in the sugar solution, and serves to maintain a constant H-ion concentration throughout a series of tests. This is very important since the amount of color adsorbed by a carbon is very sensitive to changes in acidity (or alkalinity), especially near the neutral point. It frequently happens, when testing carbons from widely different sources, that some of them will contain a small amount of acid and others, alkali. If the sugar solution be neutral or be not fortified against changes in concentration of either H or OH ion, one carbon may be

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[1] Received August 26, 1921.

[2] Published with the permission of the Secretary of Agriculture.

[3] Parts I to IV, This Journal, **11** (1919), 864; **12** (1920), 682, 786; **13** (1921), 605.

[4] This Journal, **10** (1918), 812

[5] *Ibid.*, **13** (1921), 150.

[6] *Ibid.*, **8** (1916), 519.

[7] Louisiana State Agricultural Experiment Station, *Bulletin* 167 (1919), 12.

tested in an alkaline medium and the other in acid. The results will not be comparable in the least degree.

With adjustments in concentration to suit the individual requirements, beet molasses or malt sirup may be used instead of cane molasses.

No buffer salt is required if carbons are to be tested on solutions that are strongly acid, such as concentrated citric or lactic acid.

THE APPLICATIONS OF KELPCHAR

CANE SUGAR—The sugar manufacturer is fortunate in having a choice of methods for refining his product. He may resort to either purely chemical or purely adsorptive processes, or a combination of the two. Zerban[8] has made extensive experiments with the physical methods of refining sugar, and concludes that cane juice clarification may be brought about without the use of any chemicals whatever, but simply by the use of efficient adsorbents. It was found by laboratory and factory tests that in comparison with the sulfitation process, at least the same quantity of first sugar of greatly superior quality can be made by clarification with 0.5 per cent kieselguhr, followed by treatment with 1 per cent of an active vegetable carbon, and filtering the juice in both cases, which is easily and rapidly done. The first molasses, he states, is so very light in color that the recovery of high-grade sugar can probably be materially increased, still leaving a molasses of higher market value than that made by the usual plantation methods. Essentially the same result was obtained with kelpchar.

More recent tests of this nonchemical method of preparing white sugar direct were conducted by Mr. J. F. Brewster of the Bureau of Chemistry, U. S. Department of Agriculture, and others at the Louisiana State University Experiment Station at New Orleans. Cane juice from the mill was filtered hot, first through kieselguhr to remove coarse suspended matter, then was treated with 1 per cent of carbon (ash- and moisture-free basis) calculated on the original weight of juice. These treatments were made at the Station sugar house, and may be regarded as being on a factory scale as far as the filtration is concerned. An ordinary plate and frame filter press was used. Parallel runs were made with four carbons; carbon A, an imported carbon; B and C, American carbons; and kelpchar.

Table I shows the total color remaining in the juice after treatment with kieselguhr and then with carbon. These color units were determined by means of the Hess-Ives tint photometer. Table II shows colloids remaining in the juices after treatment with kieselguhr and carbon, respectively. The results were obtained by dialyzing the juices until free from crystalloids, then evaporating to dryness, and weighing the solid residue. Results are expressed in g. per 100 cc. of juice.

TABLE I—TOTAL COLOR REMAINING IN JUICES AFTER TREATMENT

RUN No.		TOTAL COLOR	CARBON	TOTAL COLOR
1	Kieselguhr	83.17	A	13.40
2	Kieselguhr	84.56	Kelpchar	13.36
3	Kieselguhr	86.03	B	3.20
4	Kieselguhr	81.56	C	16.90

The color remaining in the juice and not that removed is regarded as determining the usefulness of the decolorizing agent, since the color remaining will appear in the sugar and molasses.

TABLE II—COLLOIDS IN JUICES AFTER TREATMENT

RUN No.		Colloids G. in 100 Cc.	CARBON	Colloids G. in 100 Cc.
1	Kieselguhr	0.0226	A	0.0111
2	Kieselguhr	0.0318	Kelpchar	0.0114
3	Kieselguhr	0.0371	B	0.0113
4	Kieselguhr	0.0333	C	0.0234

Thus, the sugar manufacturer may make white sugar direct from cane juice, or he may make brown sugar and sell to the refineries, there to be redissolved, bleached, and recrystallized. Refinery practice prescribes most commonly the use of bone-black as the bleaching agent. Kelpchar would appear to be a desirable substitute. The foregoing results, from a long list, would seem to establish beyond a peradventure the ability of kelpchar to decolorize sugar solutions. Its activity has been shown to be about twenty-five times that of bone-black. The significance of this fact will be discussed subsequently. Its use necessarily following that prescribed for active carbons, it cannot be used in percolators but must be added to the solutions and filtered out—a simple and easily standardized process.

Sugar refiners desire a charcoal that will remove inorganic substances, such as lime and iron, as well as the colored organic compounds. It is unquestionable that charcoals do adsorb inorganic material, even of low molecular weight, although in absolute units the quantity is seldom more than a few milligrams per gram of charcoal.[9] But since there is only a small percentage of inorganic material in sugar sirup, it may be that most of it likewise can be eliminated by kelpchar. No data are available for proof, but it is only reasonable to suppose that the greater the adsorptive ability of charcoal, the greater would be its tendency to remove the inorganic impurities by adsorption. The impression prevails that bone-black removes a large portion of the inorganic salts present in sugar solutions purified therewith, but records of the actual tests on which this belief is founded seem to be lacking. If these cannot be removed sufficiently by direct adsorption, they might possibly be converted into insoluble compounds which could be removed by filtration.

CARAMEL—A test solution of sugar was employed which had been colored to read 50. The percentage color removed was read as the percentage of decolorization. Comparison was made between kelpchar and two of the best known imported carbons. These are designated as "A" and "B." The former is the same carbon as that designated by the same letter in the tests on cane sugar recorded above; and, likewise, in tests on glucose given below.[10]

TABLE III—DECOLORIZATION OF CARAMEL SOLUTION

Weight of Sample Gram	KELPCHAR		CARBON A		CARBON B	
	Reading	Per cent Color Removed	Reading	Per cent Color Removed	Reading	Per cent Color Removed
0.25	11.0	78	16.5	67	19.0	62
0.50	7.5	85	10.5	79	11.0	78
0.75	5.5	89	8.0	84	8.0	84
1.00	4.5	91	7.0	86	7.0	86

GLUCOSE—The effects of various amounts of kelpchar, carbons A and B, and kieselguhr were determined on light glucose liquor as it came from the press. The decolorizing agents were added and the mixture heated for one-half hour on the steam bath, then filtered, and the colors read in a four-inch cell with yellow and red Lovibond glasses. The filtered samples were placed on ice over night and the brilliancy or haziness noted. The original liquor tested 4 yellow and 1 red. It became hazy very quickly. All solutions treated with kieselguhr became hazy.

TABLE IV—DECOLORIZATION OF LIGHT GLUCOSE LIQUORS

Per cent Material	KELPCHAR			CARBON A			CARBON B		
	Yellow	Red	Condition	Yellow	Red	Condition	Yellow	Red	Condition
0.1	3.2	1.0	Hazy						
0.2	1.2	0.3	Brilliant	0.27	0.7	(Slightly hazy)	2.0	0.2	Brilliant
0.4	0.7	0.1	Brilliant				0.9	0.1	Brilliant
0.6	0.4	0.1	Brilliant	0.8	0.2	Brilliant	0.7	0.1	Brilliant
0.8	0.2	0.1	Brilliant				0.5	0.1	Brilliant
1.0	0.2	0	Brilliant	0.7	0.1	Brilliant	0.4	0	Brilliant

With kelpchar and carbon B very brilliant liquors were obtained where 0.2 per cent or more decolorizing material was used. Below 0.2 per cent the liquor became hazy on chilling. Although in this case the only experiment performed was with 0.1 per cent kelpchar, hazy liquors were also formerly obtained when 0.1 per cent carbon B was used, whereas with 0.2 per cent carbon B the light liquor from the presses remained brilliant for several days. These experiments confirm the conclusion that 0.2 per cent activated carbons produce permanently brilliant glucose liquor. Below this amount, liquors do not remain brilliant. Kieselguhr, even up to 1 per cent, gave hazy liquors, and had but little effect on clarifying the liquors.

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[8] Louisiana State Agricultural Experiment Station, *Bulletin* **173** (1920).

[9] Osaka, *Mem. Coll. Sci. Kyoto*, **1** (1915), 257.

[10] This test and the following one on glucose were made in the Edgewater plant of the Corn Products Refining Co., and the results were submitted through the courtesy of Dr. C. E. G. Porst.

MALT SIRUP—The high prices obtainable for sugar and sugar substitutes which coincided with the inauguration of national prohibition had as a result the stimulation of interest in the manufacture of malt sirup as a product to which breweries and distilleries could be applied. Malt sirup is naturally yellow or brown in color, due to the presence of such substances as chlorophyll, polyphenols, iron and caramel, and it finds a more ready acceptance and a less restricted use if decolorized. Its bleaching proved a more difficult matter than that of cane sugar. Quantities of kelpchar sufficient to bleach to absolute colorlessness a solution of cane molasses of an equal intensity of color still left perceptible yellows in the solutions of malt sirup. In addition, colloidal materials, some of them of the nature of peptones and albumens, which slowly precipitated and caused a reversion to haziness, were likewise removable by kelpchar.

In testing the activity of kelpchar as a bleaching agent for malt sirup, the following method has been recommended:

To 1 kg. of sirup add 2200 cc. water. After thorough mixing the Brix reading should be 25° (sp. gr. 1.106 at 17.5° C.), a variation of 1° either way being allowable. To a liter of this solution 20 g. of the carbon to be tested are added, and the whole placed on a water bath where it is brought to a temperature of 90° C. and permitted to remain thereat for 20 min. It is filtered through double filter papers, the filtrate being returned if not clear. The filtrate is then compared colorimetrically with the original solution, with a Schreiner or other colorimeter. The color should be reduced to 95 per cent of its original intensity. The volumes may be varied to suit the convenience of the operator.

For malt sirup a certain latitude in characteristics of the carbon is allowable. Thus water-soluble sulfates and chlorides of the alkalies and alkaline earths are permissible to the extent of 1 per cent, and free hydrochloric or sulfuric acid to the extent of 0.2 per cent. The carbon must be acid or neutral.

CITRIC ACID—In the manufacture of citric acid from lemons, the product is colored even after the acid has been precipitated as calcium citrate from the original juice and filtered, and the acid liberated again with sulfuric acid. Sufficient coloring matter is carried through the process to leave the solution dark brown and to require bleaching. The coloring matter here present is for the most part of the sort that can be adsorbed with carbons. However, in most cases enough iron salts are taken up during the process of manufacture to impart a distinct coloration on its own account. The ferric ion is not readily adsorbed from such solutions and it is, therefore, precipitated as the ferrocyanide. For the removal of the other coloring matter kelpchar is ideal, its efficacy having been established by laboratory and plant tests, and likewise by its application over a considerable period of time as the adopted plant reagent of a large citric acid manufactory.

The requirements of a carbon for the decolorization of citric acid are rigorous. Since an acid is sought of the purity prescribed by the U. S. P., it is essential that no impurity be taken up from the carbon. Therefore, the carbon must contain no alkalies, magnesium salts, or other soluble ash constituents. It must be free from hydrochloric acid and must not contain more than a trace of sulfuric acid. A small amount of calcium sulfate is allowable, but traces of iron or other things which will impart color are prohibited. There are few applications of carbons where more strict requirements are to be met.

OILS—Glick[11] has studied the action of different charcoals on a number of vegetable oils and finds that, with the exception of coconut oil, a mixture of fuller's earth and charcoal is more effective than fuller's earth alone. Charcoal alone is better on coconut oil.

The application of kelpchar to the purification of oils is a field in which but little work has been done, but the results obtained already indicate a potentially wide usefulness for this reagent in the oil industries. The mobility of the liquid to which the carbon is applied being a factor in the rate of reaction, the more viscous oils are the more difficult to bleach. Thus, the results obtained with oils are apt to be disappointing when compared with those obtained with aqueous solutions. It is only when the various decolorizing agents for oils are compared that the value of kelpchar is shown. However, it has been shown to effect a marked improvement in some classes of mineral oils where it both lightens the color and increases the brilliancy, and a moderate application to specimens of yellow gasoline and distillate rendered them entirely colorless.

DYE INTERMEDIATES—Starting with the purest of chemicals and with elaborate control of the reactions in preparing an intermediate, it is seldom possible to prevent entirely the formation of tars. Consequently the intermediates must be purified. The final purification is usually by distillation or recrystallization, but these methods are not always as effective as desired. Adsorbents such as bone charcoal and fuller's earth have been used to some extent to remove the tars, but their low activity has prevented their wide application. On the other hand, kelpchar because of its great activity has been found to be highly efficacious in this respect.

A quantity of impure aniline, for example, which showed a pronounced orange-red color was heated to the boiling point with 2 per cent by weight of kelpchar and immediately filtered. This eliminated the orange tint. The purified aniline was diazotized and coupled with β-naphthol, and the product filtered and dried. It was decidedly more brilliant and of a purer shade of red than the same pigment made from the unpurified aniline. A further improvement was obtained when the β-naphthol solution (in sodium carbonate) was likewise purified by treating with kelpchar. Also, crude *o*-toluidine, xylidine, and *p*-nitroaniline[12] were purified, the former two by the method applied to aniline. In the purification of *p*-nitroaniline, 100 g. of the material were dissolved in hot 30 per cent H_2SO_4, 2 g. of kelpchar added, and the mixture filtered. The filtrate was added to a large volume of water, and the precipitated *p*-nitroaniline filtered off and dried. The appearance of the product was greatly improved, and when coupled with β-naphthol it gave a product that was far more brilliant than that produced by a similar process of purification without the use of kelpchar.

PRECIPITATION OF METALS—That charcoal precipitates gold from solutions of its haloid salts has long been known,[13] and commercial application was made of this principle at some plants formerly using the chlorine process for extracting gold from its ores.[14] Since 1888 chlorination has been gradually displaced by the cyanide process, in which gold is dissolved from ore as potassium or sodium aurocyanide $KAu(CN)_2$.

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[11] *Cotton Oil Press*, **4** (1921), No. 10, 41.

[12] Contributed through the courtesy of E. I. du Pont de Nemours & Co.

[13] Wm. Henry, "An Epitome of Chemistry," London, **1801**, 95, Wetlen, *Ann.*, **55** (1845), 241; **59** (1846), 354.

[14] Sir T. K. Rose, "Metallurgy of Gold," 6th Ed.. **1919**, 310.

On the large scale this gold is usually recovered from the highly dilute solution (commonly from one to ten parts gold per million) by metallic zinc in the form of shavings or dust, but charcoal has been employed to some extent as a precipitant in Australia and New Zealand.[15]

The comparison of kelpchar with other charcoals and with zinc dust as a precipitant of gold from cyanide solutions was made by Dr. W. J. Sharwood of the Homestake Mining Co., Lead, S. D., through whose courtesy the following statement of results has been made possible.[16]

TABLE V—PRECIPITATION OF GOLD FROM CYANIDE SOLUTION BY CHARCOALS AND ZINC DUST

Grams to 300 Cc.	PRECIPITANT	Percentage Pptd. of Original Gold
0.5	Graphite, powdered	None
0.5	Old pine charcoal, 100-mesh	None
0.5	Reheated pine charcoal, 100-mesh	95.0
0.5	Peach-pit charcoal, 100-mesh	90.7
0.5	Kelp charcoal sifted through 100-mesh, coarse rejected	70.0
0.3	Old pine charcoal, 100-mesh	None
0.3	Reheated pine charcoal, 100-mesh	85.8
0.3	Peach-pit charcoal, 100-mesh	80.3
0.3	Kelp charcoal, unsifted, only 5-min. contact, preliminary test	40.3
0.3	Kelp charcoal, 100-mesh	53.7
0.3	Kelp charcoal, 100-mesh	55.2
0.3	Kelp charcoal, reheated, 100-mesh	84.9
0.3	Special zinc dust, 300-mesh	73.0
0.1	Special zinc dust, 300-mesh	38.1
0.03	Special zinc dust, 300-mesh	5.0

It may be of interest to note here that similar zinc dust, when used on a very large scale in still smaller proportions than in the last test, 0.004 to 0.005 per cent of the weight of solution carrying $4.00 to $6.00 gold per ton (7 to 10 parts gold per million), the zinc being added at the moment of pumping to a filter press, regularly precipitates 99.8 per cent of the gold contents. Comparing this with the above results makes it seem probable that kelpchar, if applied under favorable conditions, might show a greater efficiency as a gold precipitant than these small-scale tests indicate.

These tests were made on a cyanide mill solution whose gold value was about $4.20 per ton. Agitation was effected by shaking for exactly 10 min. in a mechanical shaker with a horizontal throw of 2 in. and at a speed of 240 r. p. m. The solution was contained in bottles of 360-cc. capacity. After shaking, it was filtered only once.

Qualitatively, kelpchar likewise precipitates gold rapidly from haloid solutions.

Seemingly, what is being dealt with in these experiments is not activity of decolorizing carbons as that term is understood in the other parts of this paper. Since charcoals of no recognized ability as decolorizing carbons are more efficient precipitants for gold than kelpchar, it is obvious that the function here recorded is of a different order from that to which kelpchar owes its value.

OTHER APPLICATIONS—The efficacy of kelpchar has been demonstrated in the bleaching of lactic acid; vinegar; molasses for the growing of white yeast; glycerol; grape, and other fruit juices, and fruit sirups and concentrates; honey; potassium tartrate and tartaric acid; phosphoric acid; photographic chemicals; alkaloids; and pharmaceuticals.

The proposed applications for kelpchar are numerous and are promising of usefulness. The stability of explosives could probably be enhanced through the removal by kelpchar of those impurities, such as the highly nitrated phenolic compounds in TNT[17] which contribute to instability. The relationship between adsorption and surface phenomena suggests the use of kelpchar as a contact or catalytic agent to induce desired reactions.[18] The catalytic action of active carbons in reactions between gases is illustrated by their use in the formation of carbon tetrachloride from chlorine and natural gas. It should prove of value in promoting reactions in both gaseous and liquid media. The adsorption of bacteria from solutions with active carbons should be a simple matter and more nearly quantitative with a carbon of the activity of kelpchar. Likewise the results obtained from the internal application of charcoal to correct digestive disorders should be much more pronounced where active carbons of the order of kelpchar are used. Its application in the field of gas-absorbing charcoals is now under investigation.

REACTIVATION OF KELPCHAR

The restoration of the decolorizing power of kelpchar has been effected satisfactorily by the established methods of reactivating carbons, and, in addition, new and original processes of accomplishing that purpose have been developed.

Numerous processes have been described and patents granted for reactivating spent carbons, but the principles involved are few. What is desired essentially is the removal of the coloring matter and other impurities which have saturated the adsorptive capacity of the carbons. Their removal is accomplished by heating the carbon to a temperature which effects their volatilization, or, more commonly, their destructive distillation and possibly the simultaneous activation of any residual carbon remaining after their distillation. Or, where the chemical nature of the adsorbed impurities is understood, the carbon may be treated with some reagent which will enter into combination with the impurities to form compounds more soluble, so that they can be washed out without a change of medium. Or, they may be oxidized by the application of an oxidizing agent of the nature of chromate or permanganate. This likewise presupposes an understanding of the nature of the compounds to be removed.

The reactivation of vegetable carbons by heating naturally suggests itself, since that is the conventional method of reactivating bone-black. The bone-black is washed, dried, and fed by gravity through vertical retorts. The granular nature of the material and its relatively high density makes this possible. The high percentage of ash, also, reduces the tendency to oxidation and consequent loss. Vertical retorts have not been found to be wholly applicable to the reactivation of vegetable carbons, however, since they are pulverulent and of low density and do not readily flow through a vertical retort of the diameter required for efficient heating. Horizontal retorts and mechanical conveying, accordingly, have been adopted.

The disadvantages of this method of reactivation are pronounced. The carbon must be dried, and to transport the carbon from the filter, where separated, and prepare it for re-burning requires considerable manipulation and time. The retorts are expensive to construct and to operate. Being made of cast iron and being maintained at the temperature required for reactivation (a red heat), they are easily damaged and readily deteriorate. It is difficult to prevent the escape of dust and the consequent disfigurement of the plant. The method has little more than precedent to recommend it. However, the cost involved where active carbons are being used, while per unit weight no greater, per unit of activity is vastly less. If such an expense for reactivation is allowable where bone-black is the reagent used, it is relatively insignificant where active carbons are employed.

The following method has been applied to the reactivation of kelpchar with entire success: First, on the laboratory scale, kelpchar was saturated with the impurities contained in cane molasses, and was then washed, dried, and retorted at 800° C. It was then cooled, washed with dilute hydrochloric acid and then with water, and dried. Its activity had been completely restored. Subsequently, users of kelpchar reported that they had repeatedly reactivated it by this method in an entirely satisfactory manner.

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[15] W. D. Johnston, U. S. Patent 522,260 (1894); W. H. Gaze, "Practical Cyanide Operations," London, 1898, 13 and 121; *Chem. Eng. Min. Rev.*, **10** (1917), 48; *Chem. Met. Eng.*, **18** (1918), 642.

[16] See also Clark & Sharwood, *J. Chem. Met. Soc. S. Africa*, **10** (1910), 234.

[17] Weiss, THIS JOURNAL, **10** (1918), 1028.

[18] THIS JOURNAL, **11** (1919), 639.

WET METHODS—The better known of the wet methods of reactivation is the one prescribing the use of a caustic wash. Lime, caustic soda, and soda ash are the alkalies recommended. Where these unite with the coloring matter adsorbed on the carbon to form compounds much more soluble than the coloring matter uncombined, their use is efficacious. Thus, in the bleaching of sugar, the coloring matter is made up principally of phenolic compounds, which form highly soluble salts with caustic soda, and these salts are easily washed off with water. Similarly, basic pigments are removable with an acid wash. The principle is applicable where the chemical nature of the pigment is known. While this method is applied commercially to only a limited extent, it offers some distinct advantages in the saving of the cost, maintenance and operation of retorts, loss of carbon through combustion, and the elimination of dust. In the proposed automatic and countercurrent application of kelpchar,[19] the apparatus for the reactivation of the carbon would be similar in principle and possibly in design to that used in its application as a bleaching agent, and could easily be a continuation of it. The costs involved for caustic, acid, and water, and for operating the apparatus, would not be excessive. It has much to recommend its further study and application.

Kelpchar has been reactivated as follows: A portion of the material which had been saturated with the coloring matter adsorbed from cane molasses was washed with a dilute solution of caustic soda. After washing to remove the excess of caustic, and treating with hydrochloric acid and then with water to restore neutrality, the carbon was dried. It was found to have regained entirely its original activity.

CHEMICAL METHODS—The strictly chemical methods of reactivation offer a wide field for research. It remains only to determine the chemical identity of the compounds saturating the spent carbon, whereupon reagents which will oxidize or reduce or otherwise alter or destroy them or render them soluble can be discovered and applied. They can be applied countercurrentwise so as to insure their efficient use, and their application can be made entirely automatic.

The electrolysis of an acid, alkaline, or neutral salt solution either in anode or cathode compartment, or without diaphragm, carrying a suspension of the kelpchar would result in the liberation of electrolytic products of a nature to oxidize or reduce the materials to be removed from the carbon. In addition, there would be the tendency of the coloring matter to migrate under the influence of the electric current away from the carbon.

Little work, also, has been reported on methods involving a change in medium. Compounds of sufficiently low solubility to admit of their being adsorbed from water solution might be so soluble in some other medium, such as alcohol, solvent naphtha, or benzene, as to make possible their removal by washing with such a liquid. The destruction and removal of the organic matter on the carbon by fermentation has been suggested and shown to be applicable,[20] but is restricted to those compounds that are fermentable.

In short, while the best known method of reactivating kelpchar in particular and decolorizing carbons in general, the retort method, is efficacious and economical and answers the requirements of the moment, it would appear to be destined to yield to more exact and efficient methods. The potential advantages of the wet methods are such as to warrant their prompt and elaborate study.

IMPORTANT CHARACTERISTICS OF A GOOD DECOLORIZING CARBON

ACTIVITY OR ADSORPTIVE CAPACITY—By the activity of a carbon is meant its ability to remove coloring matter or other impurity from a liquid. The greater the activity, the smaller the amount required for a given result. The greater the activity, other things being equal, the greater the intrinsic value. A reduction in the quantity of carbon reduces the floor space and size of filters required, affording a saving in the initial cost of buildings and apparatus, decreases the operating costs for filter cloths, labor and repairs, and increases output. With a very slight increase in the amount of carbon used, greater decolorization of the solution may be had which, in the case of a crystalline product, means less washing of the crystals on the centrifugals. A smaller quantity of carbon means a smaller loss of product in the filter cake, and a smaller consumption of wash water. Only a small amount of carbon has to be handled in the reactivation apparatus, there being an attendant saving in both installation and operation. This cost being so much per pound, it should be inversely proportional to the activity. This is of especial importance, as the cost of reactivating bone-black, for example, represents a heavy expense in the aggregate.

Since adsorptive capacity is certainly the most important characteristic of a decolorizing carbon, it is inevitable that such carbons will be purchased in terms of their activity, at so much per unit of activity. The procedure in use in the buying of potash salts, coal, and numberless other commodities purchased on the basis of analysis and intrinsic value has not been established in the purchase of carbons. In arriving at a price which he is willing to pay, the purchaser is inclined to take bone-black as the standard, but considers the unit of weight rather than the unit of activity. At present no unit of activity has been established, but this only awaits the prosecution of some greatly needed researches to that end. When it is established, kelpchar, which on analysis shows an activity twenty-five times that of bone-black, will bring a price twenty-five times that of bone-black. Furthermore, processes of manufacture developed for kelpchar which make it possible to produce grades of greatly increased activity over that now produced will be put into practice, where now in the absence of a fair appreciation of higher degrees of activity only the lower grades can with profit be manufactured.

SIZE OF PARTICLES—The higher degrees of activity are obtainable only with certain degrees of fineness. The ideal of a carbon coarse enough to admit of percolation and possessing the activity of kelpchar does not seem to be attainable. Adsorption being a surface phenomenon, either a fine state of division or extreme porosity is a prerequisite.

Assuming the same degree of effective activity, the coarser a carbon is, the better, since it is more readily filtered from a solution. Filtration is more rapid and a heavier filter cake is allowable on the filters, and a coarser filter medium can be used. Conversely, the finer a carbon is, assuming the same shape of carbon particle, the sooner will a filter become clogged and the more often must the filtering operation be interrupted. As an aid to filtration, coarser materials, such as kieselguhr, are sometimes added with the carbon. But the logical way to overcome the difficulty is to use filters which make automatic or at least easy the frequent breaking and removal of the filter cake. The rotary vacuum and the centrifugal filters in many applications are ideal for this purpose.

The degree of fineness of kelpchar is determined largely by the method of manufacture. While fine, it is remarkably free-filtering. A typical specimen on analysis showed a physical composition such that 9 per cent was retained on a

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[19] THIS JOURNAL, 13 (1921), 605.

[20] *J. Soc. Chem. Ind.*, 16 (1903), 565.

20-mesh sieve; 17.8 per cent on a 40-mesh; 19 per cent on a 60-mesh; 5.5 per cent on an 80-mesh; 5.4 per cent on a 100-mesh; 44 per cent passing the last named.

With the development of the art it might prove advantageous to screen to uniform sizes. On the other hand, the presence of coarse particles assists in the removal of the finer.

SHAPE OF PARTICLE—Size of particle is not the sole factor determining filterability. Much depends on the shape, since the rate of filtration depends on the maintenance of open interstices between the particles, yet wide differences in filterability are noted where it is not possible to observe under the microscope a difference in shape of particle to account for them.

HARDNESS OF PARTICLES—While it is hoped that a carbon will be offered the trade which is both highly active and at the same time cheap enough to warrant its being thrown away after one usage, the probabilities are that the cost of reactivating will always be less than that of manufacturing. If carbons are to be used repeatedly, unless their particles are hard they will break down under repeated handling and eventually be objectionably fine. On the other hand, the harder the particle, the more abrasive the carbon is and the shorter will be the life of the apparatus used in handling it. The latter is the more serious objection. It is easier to design apparatus which will handle the carbon without unduly breaking down the particles than it is to find materials of construction which will withstand abrasive action. Here is an excellent field for engineering research.

ABSENCE OF SOLUBLE IMPURITIES—Carbons of vegetable origin contain residues of the inorganic constituents of vegetable matter. Thus, there may be expected small amounts of calcium, magnesium, and iron, the amount depending on the process of manufacture. The calcium may be expected in the form of sulfate since in this form it is the more difficult to remove. The presence of sulfates leads to the formation of sulfides and free sulfur through their reduction. Since the preparation of carbon from activated charcoal consists essentially in the removal of these impurities with both acid and water, the amount in which they are present depends on the thoroughness with which it has been refined. Small amounts of free acid may likewise remain.

Insoluble impurities are objectionable only as diluents. The soluble ones are objectionable in the product if they interfere with subsequent crystallization, as may calcium sulfate; or, if they add color, as may iron compounds; or, if they add unduly to the impurity of the product, as all of them may. Free sulfur may be taken up by oils and their color, taste, and odor altered. The ease with which sulfur may be removed from carbons leaves no justification for its presence. Free acid acts on certain coloring matter possessing the characteristics of indicators, changing their color and in cases affording a false bleaching action. The presence of an excess of acid in carbons applied to sugar may induce inversion. On the other hand, the presence of acid may depress the solubility of the impurity to be removed, and thus be of material aid. Where it increases this solubility it is correspondingly objectionable.

SUMMARY

A simplified method of testing decolorizing carbons has been given.

Results are reported of laboratory and plant-scale tests of kelpchar used as a decolorizing agent applied to numerous materials and new uses are suggested.

Methods of reactivating spent carbons are discussed.

The important characteristics of decolorizing carbons are detailed.

Determination of Monobromated Camphor[1,2,3]

By Elgar O. Eaton

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

The need of quantitative method for determining monobromated camphor arose some time ago in connection with the analysis of tablets, prior to the appearance of Emery's procedure for the estimation of this substance in migraine tablets.[4] The literature available in this laboratory having failed to disclose any finished method directly suited to the problem, attention was directed to a statement made in Schmidt's "Pharmaceutische Chemie,"[5] to the effect that silver oxide decomposes monobromated camphor in the presence of chloroform into silver bromide and other products. Some preliminary experiments showed that the mixture resulting from the addition of 0.5 *N* alcoholic potassium hydroxide to alcoholic silver nitrate, and containing among other things silver oxide, constitutes an ideal solvent for monobromated camphor, and hence a more rational medium in which to bring about the desired reaction, since it eliminates the possibility of chloride formation, as would be the case if chloroform were used.

METHOD

To an amount of the uniformly powdered sample equivalent to about 0.2 g. of monobromated camphor, accurately weighed into a small beaker, add 25 cc. alcohol, warm on the steam bath, filter into a flask, wash both beaker and filter with warm alcohol until all the camphor derivative is removed, add 50 cc. 0.5 *N* alcoholic potassium hydroxide, follow with 25 cc. of alcoholic silver nitrate (0.2 g. in 50 cc. alcohol), connect with a ground-on reflux after the addition of a few glass beads, and boil gently 1.5 hrs., adding at intervals through the condenser the remainder (25 cc.) of the alcoholic silver nitrate. Cool, disconnect, and transfer contents to a large porcelain evaporating dish. Dilute with water to 200 cc. and decant into a beaker, washing the precipitate with water by decantation. Boil the aqueous-alcoholic solution 5 min. with 1 g. of zinc dust in order to clarify it, filter into another beaker, washing thoroughly with water, and add dilute nitric acid to decided acidity and aqueous silver nitrate to complete precipitation. Determine bromides by the usual gravimetric method. (Factor for monobromated camphor = 1.23.)

The special apparatus consists of a 250-cc. flask with ground-on condenser. This is not imperative but if available should be used.

RESULTS

The following results were obtained with this procedure:

SAMPLE	PER CENT
Commercial monobromated camphor....	98.4, 95.8, 96.9, 99.9
Uncoated tablet, labeled 3 grs...........	2.77, 2.77, 2.82
Sugar-coated tablet, labeled 5 grs........	4.71, 4.78

It was found that the addition of more water lowered the results, and that it was advantageous to add the alcoholic silver nitrate in several portions through the condenser to the hot alcoholic potash solution rather than to apply all the silver salt at one time. It is possible that, after the silver oxide becomes agglutinated, the catalytic action, to which the reaction appears to be due, is at an end. It was further shown that potassium bromide is formed and not silver bromide, also that no bromate is produced.

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[1] Received July 13, 1921.

[2] Published by permission of the Secretary of Agriculture.

[3] This article has been reviewed by Dr. W. O. Emery prior to publication.

[4] THIS JOURNAL, **11** (1919), 756.

[5] II, Vol. 2 (1911), 1393.

Reactions of Accelerators during Vulcanization. IV—Mechanism of the Action of Zinc Compounds[1]

By C. W. Bedford and L. B. Sebrell

Research Laboratories, Goodyear Tire & Rubber Co., Akron, Ohio

In the preceding paper of this series[2] the mechanism of vulcanization was not discussed. The object of the present paper is to present additional data and to consider the mechanism of action of these curing agents.

Five days subsequent to the reading of our last paper Bruni and Romani read a paper[3] before the International Rubber Conference in which the experimental data corroborate and duplicate our work. It is worthy of comment that two sets of workers on opposite sides of the globe should so accurately parallel each other. This parallelism also extends to the two papers,[4] one by Bruni and one by Romani, which were recently abstracted by Schidrowitz.[5] While we gladly acknowledge the work of Bruni as independent, we feel that a few further remarks are necessary.

Bruni questions our knowledge of mercaptobenzothiazole as a sulfur reaction product of thiocarbanilide. We have been working on this as well as on many other sulfur reactions for over six years, and it was through the isolation of mercaptobenzothiazole from the sulfur reaction product of thiocarbanilide that we first became acquainted with the thiazolemercaptans, their disulfides, polysulfides, and zinc salts. These were mentioned in our last paper as being excellent accelerators, some of them at ordinary temperatures. We also mentioned the zinc salt of ethyl xanthate as an accelerator free from nitrogen and were not at that time aware that it had been previously described by Ostromuislensky. We gladly acknowledge his priority as pointed out by Bruni.

Bruni also finds that mercaptobenzothiazole is formed by heating methylenediphenyldiamine with sulfur and has evidently overlooked our earlier paper[6] wherein we stated that the first reaction product of this diamine is thiocarbanilide. Since this is true, the ultimate reaction product should be the same. We verified this prior to January 6, 1917, at which time we applied for our American patents[7] which have recently been issued. The corresponding British patent[8] has been published for some time.[9]

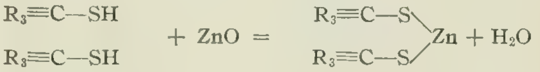
The discovery of tetramethylthiuram disulfide as an accelerator and curing agent is also claimed by Bruni. This accelerator has been on the market in this country for about three years and enjoyed secret commercial use for several years prior to public sale. The availability of its sulfur for vulcanization had been noted by us and by several other investigators, although Bruni was the first to publish the information.

Mechanism of Acceleration

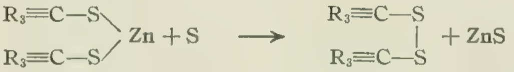
The experimental data published by Bruni exactly duplicate a portion of our work; yet we find that we materially differ from him as to the theory for the mechanism of the vulcanization reactions. We seek, therefore, by the aid of additional data, not to disprove but rather to qualify and enlarge upon his theories. Applied to thiocarbanilide the Bruni mechanism may be represented by the following equations:

Thiocarbanilide + heat = Phenyl mustard oil + aniline (1)
Phenyl mustard oil + sulfur = Mercaptobenzothiazole (2)
Mercaptobenzothiazole + ZnO = Zinc mercaptide + H_2O (3)
Zinc mercaptide + sulfur = Mercaptobenzothiazole disulfide + ZnS (4)
Disulfide + heat = Monosulfide + sulfur available for vulcanization (5)

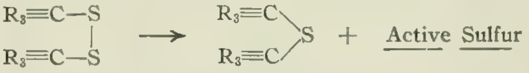
The last equation represents the general theory which Bruni applies to thiurams, dioxónthiogens and to other accelerators in general. The proposed mechanism may therefore be represented as follows:



(6)



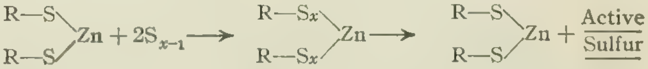
(7)



(8)

The theories which the present writers have proposed in the past and now wish to amplify are somewhat different. Using zinc as a representative of all metals which function similarly, we have three variations of the mechanism of vulcanization to propose. All of them are based on our original theory of polysulfides.

1—The action of metallic salts of mercaptans, dithiocarbamates, carbamates, xanthates, thioureas, etc., is represented thus:



2—The action of inorganic accelerators such as zinc oxide, litharge, lime, etc., also proceeds through polysulfides in absence of organic accelerators which produce carbosulfhydryl groups other than hydrogen sulfide.

$$ZnO + 2H_2S \longrightarrow Zn(SH)_2 + H_2O$$

$$y\ Zn(SH)_2 + (y-1)S \longrightarrow HS—(Zn—S—S)_{y-1}—ZnSH + (y-1)H_2S$$

$$(—Zn—S—S—)_y + yS_{x-2} \longrightarrow (ZnS_x) \longrightarrow (ZnS_2)_y$$

$$\text{or } (ZnS)_y + \underline{\overline{\text{Active}}}\ \ \underline{\text{Sulfur}}$$

A differentiation is now made between the active metallic oxides or hydrates as primary or as secondary accelerators. Where they form mercaptides or metallic persulfides their action is that of a primary accelerator. Where they speed the formation of organic sulfhydryl groups on resins, proteins, or added accelerators by removal of hydrogen sulfide, such action is purely secondary. In practically all cases both actions take place simultaneously. There is only one class of organic accelerators which acts both as primary and as secondary accelerators. We reserve the discussion of nitroso accelerators until a later date

3—Organic accelerators in absence of secondary accelerators function as follows:

$$R—H + S \longrightarrow R—SH$$

$$2RSH + S_4 \longrightarrow R—S—S—R + H_2S$$

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[1] Presented before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] This Journal, **13** (1921), 1034.

[3] *India-Rubber J.*, **62** (1921), 63.

[4] *Giorn. chim. ind. applicata*, **3** (1921), 196.

[5] *India-Rubber J.*, **62** (1921), 89.

[6] Bedford and Scott, This Journal, **12** (1920), 31.

[7] Bedford, U. S. Patents 1,371,662 (1921); 1,371,663 (1921); 1,371,664 (1921).

[8] Brit. Patent 139,857 (1919).

[9] In regard to priority on the subject of causing accelerators to react with sulfur before vulcanization, we may say further that Bruni correctly cites the Peachey patent, Brit. Patent 113,570 (1917), as prior to our British patent of 1919. Peachey specifically patented the sulfur reaction product of *p*-nitrosodimethylaniline as an accelerator and filed his application on August 23, 1917. Our first American patent was filed on January 6, 1917, in which we mentioned the sulfur reaction products used by Peachey (see page 3, line 32, U. S. P. 1,371,662). Through this patent we claim priority for the principle of causing accelerators to react with sulfur before compounding with rubber and specifically for the sulfur reaction products mentioned by Peachey and by Bruni.

$$R{-}S{-}S{-}R + S_{x-2} \longrightarrow R{-}S_x{-}R$$
$$R{-}S_x{-}R \longrightarrow R{-}S{-}S{-}R + S_{x-2} + \underline{\text{Active Sulfur}}$$

Prof. Bruni's mechanism now becomes a corollary to the above equation.

$$R{-}S{-}S{-}R \longrightarrow R{-}S{-}R + \underline{\text{Active Sulfur}}$$

4—Allowing R to represent either hydrogen, metal, or radical, the entire mechanism of vulcanization with accelerators may be summed up in one equation:

$$R{-}S_x{-}R \longrightarrow R{-}S{-}R + \underline{\text{Active Sulfur}}$$

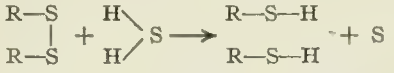
5—Without accelerators we have vulcanization by the "mother" of all polysulfides, *i. e.*, by thio-ozone itself, formed from sulfur dioxide and hydrogen sulfide.

REACTIONS OF TETRAMETHYLTHIURAM DISULFIDE

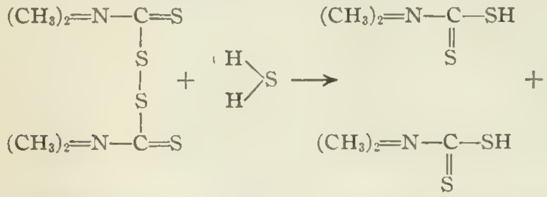
1—Bruni[10] finds that this thiuram (5 parts) with ZnO (5 parts) will vulcanize rubber (100 parts) in 15 min. at 138° C. The cure will also take place under the same conditions of mix, time, and temperature in the absence of zinc; in fact, either mix will cure in 10 min. We find the same coefficient of vulcanization in 10 min. as in 45 min. The acetone-insoluble sulfur is the same either with or without the zinc oxide, and corresponds very closely to one out of the four sulfur atoms in the thiuram disulfide. Ether-hydrochloric acid, however, removes one-fourth to one-third of the combined sulfur from the zinc stock, showing that it is present as zinc sulfide. Although the zinc stock has the higher modulus usually acquired by the addition of zinc oxide, the chemical cure has been retarded by the action of the oxide. It is important to note that in the absence of zinc oxide the sulfur which is theoretically available for vulcanization is all acetone-insoluble in the cured product.

2—This thiuram will not vulcanize a rubber-sulfur cement at ordinary temperatures either with or without zinc oxide. The sulfur of the thiuram is not available for vulcanization at low temperatures and therefore is not as active as the forms of sulfur produced by mercaptide accelerators.

3—A zinc oxide cement containing thiuram disulfide and sulfur will vulcanize on standing over night if treated with a small amount of hydrogen sulfide. Weyl[11] states that all disulfides, whether aliphatic or aromatic, are easily reduced by alcoholic K_2S or hydrogen sulfide to mercaptans, many at ordinary temperatures and more easily in the presence of bases. Free sulfur is formed.

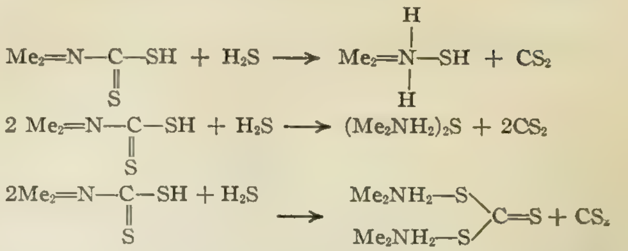


The action of hydrogen sulfide on thiuram disulfide is to reform the dithiocarbamate, which in the presence of zinc oxide again forms the zinc salt. This is a rapid vulcanization agent at ordinary temperature.



In absence of zinc oxide no cure is obtained by hydrogen sulfide and the thiuram disulfide.

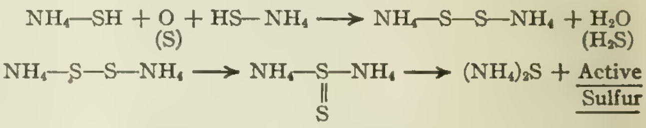
4—Thiuram disulfide in acetone at ordinary temperature reacts with hydrogen sulfide producing a cloudy precipitate of sulfur. The dimethyldithiocarbamic acid, thereby produced, reacts further with hydrogen sulfide to produce methylated ammonium sulfides or trithiocarbamates which at once redissolve the sulfur, and the final result is a deep red polysulfide solution. Some carbon disulfide is set free by these reactions.



$$Me_2{=}N{-}\underset{\underset{S}{\|}}{C}{-}SH + H_2S \longrightarrow Me_2{=}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}{-}SH + CS_2$$
$$2\ Me_2{=}N{-}\underset{\underset{S}{\|}}{C}{-}SH + H_2S \longrightarrow (Me_2NH_2)_2S + 2CS_2$$

The methylated ammonium trithiocarbonate or sulfide then forms ammonium polysulfide with the free sulfur. Extra sulfur results in a deepening of the red color.

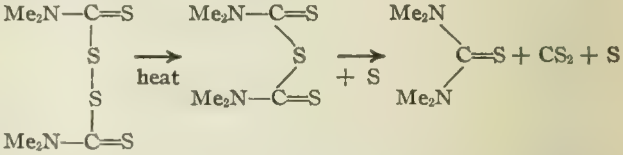
In our last paper we referred to the vulcanization of rubber by Kratz and his co-workers by the use of ammonium sulfide or hydrosulfide and invoked the aid of oxygen to form the disulfide (mono-polysulfide) since no free sulfur was present. We also stated that free sulfur would accomplish the same result. These investigators therefore deserve priority on the vulcanization of rubber by disulfides as far as publication is concerned.[12] The heat vulcanization by their method is the same as for thiuram disulfides.



$$NH_4{-}SH + \underset{(S)}{O} + HS{-}NH_4 \longrightarrow NH_4{-}S{-}S{-}NH_4 + \underset{(H_2S)}{H_2O}$$
$$NH_4{-}S{-}S{-}NH_4 \longrightarrow NH_4{-}\underset{\underset{S}{\|}}{S}{-}NH_4 \longrightarrow (NH_4)_2S + \underline{\text{Active Sulfur}}$$

In the second paper of this series,[13] the statement was made that many accelerators such as hexamethylenetetramine, *p*-phenylenediamine, and aldehyde ammonia function mainly as means for compounding ammonium polysulfides, which they generate by reaction with sulfur during the vulcanization process. A disulfide is simply the first member of the series of polysulfides.

5—Thiuram disulfide heated somewhat above its melting point turns a deep red in color, and retains this color on cooling. The writers are unable to give the exact chemistry of this reaction, but know that some dimethylamine is liberated and that the red liquid is a polysulfide, as shown by the liberation of free sulfur by acids. Romani gives the following equations:



This tetramethylthiourea has been described by Grodski[14] as a base stronger than ammonia, which liberates ammonia from its salts. The deep red solution will not vulcanize a zinc oxide cement according to all of our present tests.

6—Thiuram disulfide heated in aniline also gives a deep red solution. This solution will set a zinc oxide cement within 24 hrs. The carbon disulfide which forms reacts with aniline to produce active dithiocarbamates of zinc.

7—The action of hydrogen sulfide on thiuram disulfide in aniline at ordinary temperature produces a deep red solution. On slight heating, hydrogen sulfide is lost and the color disappears but reappears on again adding the gas. If heated higher, dimethylamine and hydrogen sulfide are lost and the color does not reappear on cooling and again adding the gas. The literature is rich in examples of the replacement of one amine by another in thioureas and dithiocarbamates. The stronger base is usually liberated. In this case we have the disulfide changed to dimethyldithiocarbamic acid with liberation of free sulfur by the hydrogen sulfide. The aniline salt of the acid then forms. Aniline then replaces the dimethylamine to form the aniline salt of phenyldithiocarbamic acid and the dimethylamine reacts with more hydrogen sulfide and sulfur to form the methylated ammonium polysulfides. The latter are broken up by heat with loss of the constituents and reformed by hydrogen sulfide as long as dimethylamine remains in the aniline.

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[10] *Loc. cit.*

[11] "Methoden der Organische Chemie," p. 243.

[12] We wish to take this opportunity to call attention to what we believe to be the first instance of the use of accelerators. Thomas Rowley, by a British patent (No. 787) in 1881, announced that rubber and sulfur would vulcanize in an atmosphere of ammonia under pressure with less sulfur than is ordinarily required. A time saving was claimed with a product less liable to subsequent deterioration. We believe that this work antedates either the work of Spence or the Bayer Co., and believe that our English brothers may therefore claim the discovery of acceleration.

[13] Scott and Bedford, THIS JOURNAL, **13** (1921), 125.

[14] *Ber.*, **14** (1881), 2754.

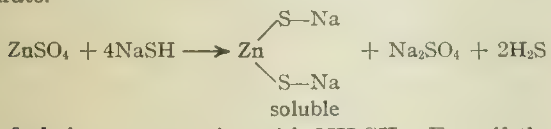
SUMMARY FOR THIURAM DISULFIDES—These disulfides contain sulfur available for vulcanization in heat cures. The presence of zinc oxide gives a higher modulus to the vulcanizate but retards the chemical cure. Thiuram disulfides, used as accelerators with sulfur in heat cures, form alkylated ammonium polysulfides and trithiocarbamates, while in the presence of zinc oxide, dithiocarbamates of zinc are also formed. In this case the zinc seems to accelerate the cure, although chemical data have not been obtained.

For low temperature cures of cements the thiuram disulfide sulfur is inactive. Zinc oxide has no effect. The addition of hydrogen sulfide to the zinc oxide cement containing the disulfide produces dithiocarbamates of zinc, and the cement quickly vulcanizes.

Reactions of Dithiocarbamates

1—Hydrogen sulfide reacts on dimethylamine-dimethyldithiocarbamate in acetone without warming, to produce alkylated ammonium sulfides and trithiocarbamates. The addition of sulfur produces a deep red polysulfide. These combinations have not vulcanized cements at room temperature.

2—Hydrogen sulfide reacts with the zinc salt of dimethyldithiocarbamic acid in aniline at ordinary temperature to produce zinc sulfide as a precipitate. As soon as this precipitate starts to form it redissolves and further hydrogen sulfide does not reform the solid. Heating forms the precipitate again. This phenomenon has its parallel in previously published data. As in the preceding example (No. 1), the carbon disulfide goes to the aniline, and dimethylamine hydrosulfide is formed with excess hydrogen sulfide. Zinc sulfide is soluble in hydrosulfides, as shown by Thomsen,[15] who added a dilute solution of zinc sulfate to a dilute solution of sodium hydrosulfide without getting a precipitate and described the solutions as analogous to the action of caustic in redissolving zinc hydrate.

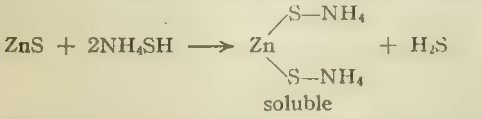


$$ZnSO_4 + 4NaSH \longrightarrow Zn\begin{matrix}\diagup S{-}Na \\ \diagdown S{-}Na\end{matrix} + Na_2SO_4 + 2H_2S$$

soluble

We find the same reaction with NH_4SH. Even if the first addition of a zinc acetate solution forms a precipitate due to local concentration, this precipitate redissolves. Hydrogen sulfide is liberated.

$$Zn(OAc)_2 + 2NH_4SH \longrightarrow ZnS + 2NH_4{-}O{-}Ac$$



$$ZnS + 2NH_4SH \longrightarrow Zn\begin{matrix}\diagup S{-}NH_4 \\ \diagdown S{-}NH_4\end{matrix} + H_2S$$

soluble

The re-solution of the zinc sulfide precipitate from the zinc dithiocarbamate in aniline is therefore due to the formation of soluble dimethylammonium dithiozincate, similar to sodium zincate. This aniline solution is bright yellow in color. Warming produces the precipitate again. With sulfur present the solution is a deep red, and this color is also lost if the precipitate is reformed by heating. We have in this case the polysulfide of a thiozincate in solution. Another instance of a soluble polysulfide of a thiozincate is found in the action of zinc acetate on Na_2S_5. With dilute solutions a large amount of the zinc salt may be added without the formation of a precipitate. This will be considered later under inorganic polysulfides. We have several times noted acetone-soluble zinc compounds in the acetone extract of vulcanized rubber stocks which were cured by the use of accelerators.

3—Zinc dithiocarbamate dissolved in aniline with sulfur in the cold and added to a pure gum cement produces a much quicker vulcanization at room temperature than when no aniline is used. The writers attribute this to the solvent action of aniline if the solution has not been heated. They are aware that others in the United States have also observed this action of aniline with zinc dithiocarbamates. In their preceding paper the writers recorded the same action of aniline on a thiocarbanilide-zinc oxide cement. They were later able to vulcanize a cement with thiocarbanilide, zinc oxide and sulfur at room temperature without the use of aniline. The reaction was slower.

4—If a solution of the above salt and sulfur in aniline (zinc salt 10 g.; sulfur 10 g.; aniline 100 g.) be heated on an electric stove, the following reactions occur:

(*a*)—A clear yellow solution results.

(*b*)—At 120° C. the liquid turns a deep red. Any precipitate formed redissolves at once. On cooling, the color is lost and a precipitate forms. Reheating causes complete solution with red color again.

(*c*)—Heated to boiling, the red color is lost and a permanent precipitate is formed. By extraction with hot benzene this precipitate is found to contain as high as 50 per cent of sulfur insoluble in solvents. This corresponds to ZnS_3 or ZnS_4. The inorganic polysulfides of zinc will be shown later to be powerful curing agents in heat cures.

The addition of this red aniline solution to a cement causes vulcanization within a few hours at low temperatures. This the writers believe to be due wholly or in part to the zinc salts of polysulfides of alkylated ammonium hydrosulfides.

In forming the aniline solution containing the permanent precipitate, dimethylamine and hydrogen sulfide are lost and thiocarbanilide is formed in solution. If this entire mix be added to a cement no vulcanization takes place after several weeks have passed.

5—The zinc dithiocarbamate boiled with sulfur in xylene at 138° C. gives only a trace of a precipitate of zinc sulfide after half an hour. Boiling for several hours precipitates the zinc, but the reaction is very slow. Both the zinc salt and the sulfur are in solution and the temperature corresponds to these used in heat cures. This is evidence that Prof. Bruni's mechanism of vulcanization through the disulfides is untenable for zinc dithiocarbamates, and also that the solvent action of aniline alone in the previous example is not sufficient to explain the increase in curing power.

In absence of other amines to take up the carbon disulfide, zinc dithiocarbamates do not readily react with sulfur to form zinc sulfide and organic disulfides. There are many cases of mercaptides of zinc, lead, and other metals forming polysulfides by treating with sulfur at ordinary temperatures, both in solution and in the dry state. The temperature factor is very important for these changes and varies greatly for different mercaptides. Even the use of different solvents is an important factor. All the evidence for the great reactivity of mercaptides as accelerators points to mercaptide polysulfides as such.

SUMMARY FOR DITHIOCARBAMATES—For low-temperature vulcanization of cements, zinc is necessary. Either zinc oxide and ammonium dithiocarbamate or the zinc dithiocarbamate may be used. Aniline is a good solvent for the zinc mercaptides and thereby speeds their action. Benzene is the most suitable solvent for the rubber.

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[15] *Ber.*, **11** (1878), 2044.

In heat cures the zinc dithiocarbamates do not easily react with sulfur to form zinc sulfide except through the further aid of hydrogen sulfide. By the action of rubber resins or proteins in producing hydrogen sulfide the zinc dithiocarbamate is decomposed into the polysulfides of substituted ammonium sulfides and trithiocarbonates, which in the presence of zinc oxide are strong curing agents. On account of the slowness of sulfur in reacting on zinc dithiocarbamates, the authors believe that hydrogen sulfide furnishes the key to a second mechanism of vulcanization by these accelerators. The primary mechanism is through the polysulfides of the zinc salts as such.

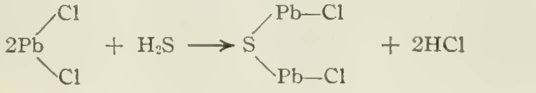
For heat cures the action of aniline is more than that of a solvent for the zinc salt. Zinc sulfides or persulfides are more easily formed and dithiocarbamates of aniline are formed rather than trithiocarbonates.

Reactions of Thiocarbanilides

1—In our previous paper we described the zinc mercaptides of thiocarbanilide and their vulcanizing powers in cements at room temperature. The temperatures required for the formation of mercaptobenzothiazole and its disulfide even in the presence of zinc oxide exclude any such mechanism for curing by thiocarbanilide at ordinary temperatures and also for heat cures at 5 lbs. of steam pressure, at which temperature we have found thiocarbanilide and zinc oxide to give a coefficient of 1.7 per cent sulfur combined with the rubber, in 5 min.

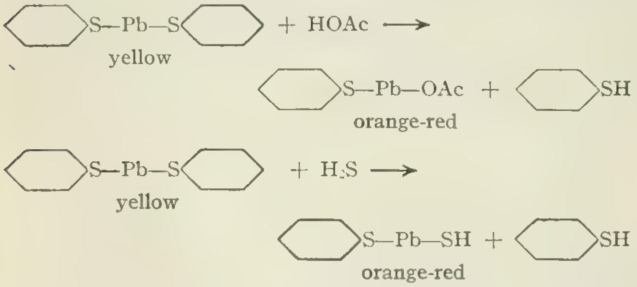
2—Litharge and lime also accelerate the curing powers of thiocarbanilide but overcure the rubber faster than when zinc is used. That this cannot be due entirely to the action of litharge, sulfur, resins, and proteins independent from thiocarbanilide is shown by the following data.

LEAD MERCAPTIDES—Renisch[16] precipitated lead salts in acid solution and obtained the sulfochloride as a red precipitate. Mellor[17] states that the precipitate may be orange, yellow or red, and gives the equation:

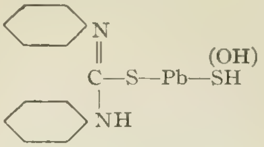


colored

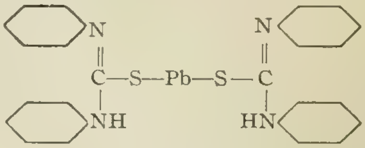
We find the same phenomena with lead thiophenol. The normal salt is a bright yellow which changes to a deep orange on adding a trace of acid or hydrogen sulfide.



A similar reaction is obtained with thiocarbanilide and litharge in benzene if chilled to 15° to 20° C. Frequent stirring for a short time produces a deep red mercaptide which is soluble in benzene and may be separated by filtration. Upon slight warming lead sulfide is precipitated from the filtrate. Under certain conditions, the writers have obtained the lead mercaptide as a clear yellow instead of red solution. From the above data they believe that the yellow solution is normal salt, while the usual red product may be called a basic salt containing a hydroxyl or sulfhydryl group on one side of the lead atom.



orange-red



yellow

The addition of sulfur to cold solutions of the lead mercaptide of thiocarbanilide results in a deepening of the red color. This is also true with other yellow mercaptides of lead. With lead thiophenol the color gradually changed from yellow through orange and red, to deeper shades down to the black lead sulfide.

3—The writers have repeated their cement experiments with aniline and carbon bisulfide, thiocarbanilide, etc., using litharge or lime in the place of zinc oxide. In every case the sulfides of lime or litharge form in a few hours and no vulcanization of the cement occurs. If the cements be chilled, the above color changes are easily observed, showing that mercaptides are first formed. By keeping the cements in the ice box we have several times observed a "livering" or partial vulcanization and in one case a permanent gel was formed.

Lead and lime mercaptides are therefore more easily amenable to the formation of disulfides than are the zinc compounds, yet no vulcanization takes place at ordinary temperatures. This is not in accord with Bruni's theory, from which we would expect greater reactivity in this case.

4—The writers have also investigated the curing power of several other lead mercaptides. Lead xanthate is a beautiful maroon compound which changes to lead sulfide before it can be mixed with rubber. The lead salt of phenyldithiocarbamic acid is comparatively stable, and lead mercaptobenzothiazole is more so. The latter will vulcanize cements at room temperatures as does the zinc salt. The cement becomes deep maroon in color, owing to the formation of polysulfides of the salt, and retains this color for weeks after vulcanization has taken place. Lead sulfide forms in a thin layer on the side of the bottle exposed to light but even this does not form for several weeks. The mechanism of vulcanization in this case is through the polysulfides of the mercaptide without the formation of lead sulfide. Moreover the red color cannot be attributed to inorganic lead persulfides, which have been shown by Schiff[18] to be unstable at ordinary temperatures.

The relative curing powers of inorganic accelerators as well as their compatibility or incompatibility with organic accelerators is therefore to be explained by the relative stability of the polysulfides of their mercaptides and sulfides. Bruni recognizes this important item by stating that "the superiority of zinc oxide towards all other metallic oxides is obviously dependent upon the conditions of stability and the decompositions of the various salts and sulfides," but fails to note the importance of the temperature factor or to recognize the metallic polysulfides, both organic and inorganic, as being the important curing agents rather than the organic disulfides.

MECHANISM FOR HIGH TEMPERATURE VULCANIZATION WITHOUT METALLIC OXIDES—For heat cures, and especially for Bruni's "ultra-accelerators," we are forced to invoke the mechanism of the mercaptide polysulfides as described above. Where inorganic accelerators are not used, we rely on the polysulfides of the disulfides until the total available sulfur becomes low and then we call on the disulfide to give up its sulfur. The assumption that disulfides give up half their sulfur to the rubber is further supported by the following references:

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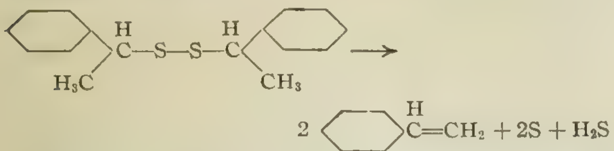
[16] *J. prakt. Chem.*, **13**, 130.

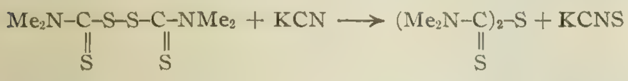
[17] "Modern Inorganic Chemistry," **1919**, 411.

[18] *Ann.*, **115** (1860), 74.

Baumann and Fromm[19] describe the heat decomposition of the disulfide derived from α-phenylethylmercaptan with the liberation of free sulfur.



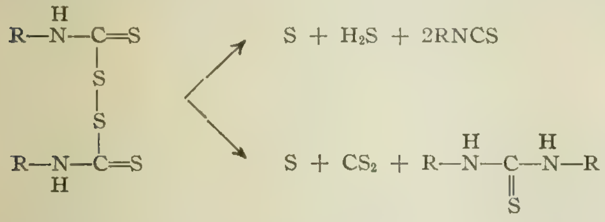
Braun and Stechele[20] obtained a theoretical decomposition of tetramethylthiuram disulfide to monosulfide by warming a suspension of the disulfide in a water-alcohol solution of potassium cyanide.



$$\mathrm{Me_2N{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}{-}NMe_2 + KCN \longrightarrow (Me_2N{-}\underset{\underset{S}{\|}}{C})_2{-}S + KCNS}$$

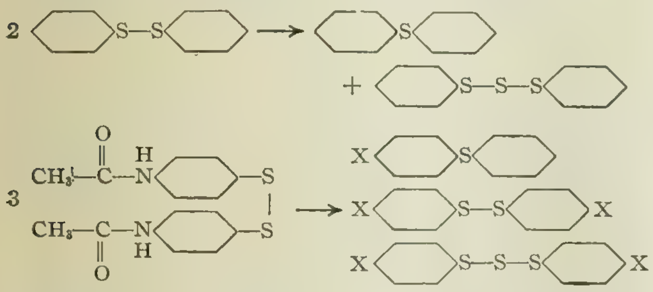
They also obtained this same result with dipiperidylthiuram disulfide, tetrapropylthiuram disulfide and with isothiuram disulfides.

Braun[21] describes the heat decomposition of disubstituted thiuram disulfides by two equations, the first one favoring aliphatic and the second favoring aromatic compounds. Both equations show the liberation of free sulfur.



Braun also mentions[22] the heat decomposition of dixanthogenides with the liberation of free sulfur.

Hinsberg[23] gives an interesting heat decomposition of aromatic disulfides which shows both their liberation of free sulfur as well equaas their ability of forming higher polysulfides.

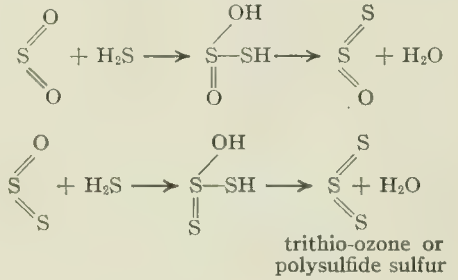


Mercaptobenzothiazole forms a disulfide when heated with sulfur. If extra sulfur is present there is a colloidal polysulfide formed which is deep red in color while hot and cools to a reddish brown resin with a conchoidal fracture. Solvents extract only small amounts of sulfur, and the polysulfide is a rapid curing agent without other free sulfur. Cold caustic soda extracts a small amount of unchanged mercaptans. According to Weyl[24] sodium sulfide forms the mercaptans without the sulfinates. The free mercaptobenzothiazole in absence of zinc oxide is a relatively poor accelerator and the disulfide or its polysulfide is still lower in curing power. This observation is contrary to the Bruni theory that disulfides are the most active form of accelerators.

Research with disulfides should be extended to dithioaniline and other disulfides.

It has frequently been noted that aniline is a stronger accelerator than thiocarbanilide in absence of secondary accelerators. Scott and Bedford proposed a reaction of amino groups with hydrogen sulfide to form derivatives of ammonium polysulfide. Sufficient experimental evidence is still lacking, and the action of organic accelerators in absence of inorganic accelerators is still virgin soil available for pioneering research.

Hydrogen sulfide decomposes many polysulfides and disulfides, such as the thiuram disulfides, with liberation of the sulfur of the hydrogen sulfide. This sulfur may therefore be considered as in the nascent state. When inorganic accelerators are used, they fix this hydrogen sulfide as metallic sulfides, as shown by W. J. Kelly.[25] In absence of these inorganic accelerators there is the possibility that the above described "nascent" sulfur is available for vulcanization. Sufficient experimental evidence is lacking to prove this point. In fact, hydrogen sulfide on nitroso compounds and other inorganic compounds liberates sulfur; yet this reaction will not vulcanize cements at ordinary temperatures. The action of sulfur dioxide and hydrogen sulfide in low-temperature vulcanization has been described as due to nascent sulfur and also as due to the formation of thio-ozone, which is simply one form of polysulfide sulfur.



The writers have evidence that the reactivity of the sulfur liberated by Peachey's process is not due to a nascent condition but to a new and active form of sulfur, which to their knowledge has not previously been described. If properly prepared, this sulfur retains its activity in vulcanizing rubber at ordinary temperature in absence of the gases from which it is formed.

If sulfur dioxide and hydrogen sulfide are passed into solvents such as benzene or carbon disulfide, cooled to 10° C. or lower, the liberation of free sulfur begins almost immediately. After sufficient sulfur has been formed one of the two gases is interrupted and the other gas passed in for an hour or longer. The sulfur, so precipitated, is bright yellow in color and on standing changes to plastic sulfur which has the same properties as when formed by pouring molten sulfur into water. On further standing, the product crystallizes.

By pouring off the supernatant liquid and washing the sulfur free from unchanged gas by cold solvent, we find that we have an active form of sulfur which if beaten into a chilled cement will vulcanize the same at low temperatures. The speedy reaction of the two gases at 10° C. or lower to liberate sulfur leads us to believe that none of the intermediate thio acids are stable at these low temperatures. Long treatment with excess of one of the gases and washing with cold solvent removes the remaining gas.

The writers therefore believe that they have isolated a new and active form of sulfur which will vulcanize rubber at low temperatures without the presence of organic or inorganic accelerators and which is trithio-ozone, or the "mother" of polysulfide sulfur itself.

There is no evidence that "nascent" sulfur is active. Further evidence on the liberation of free sulfur in rubber by various chemical reactions should prove or disprove our theory that the molecular form of the sulfur as liberated is the factor which determines its reactivity rather than the nascent condition of freshly formed sulfur.

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[19] *Ber.*, **28** (1895), 907.

[20] *Ibid.*, **36** (1903), 2275.

[21] *Ibid.*, **35** (1902), 817.

[22] *Ibid.*, **45** (1912), 2188.

[23] *Ibid.*, **43** (1910), 1874.

[24] *Loc. cit.*

[25] "The Determination of True Free Sulfur and True Coefficient of Vulcanization of Vulcanized Rubber—II." Presented at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

SUMMARY ON THIOCARBANILIDES—Thiocarbanilide functions as a mercaptan. Its zinc and lead mercaptides have been described and their polysulfides are believed to be the true curing agents. This reaction is operative for the low-temperature curing of cements as well as in heat cures. Hydrogen sulfide changes mercaptides to metallic sulfides and regenerates the mercaptan which again reacts with the metallic oxide to form the mercaptide.

The action of sulfur on mercaptans to form disulfide polysulfides is apparently inoperative for thiocarbanilide. The action of sulfur on the zinc mercaptide of thiocarbanilide is believed to function only through the formation of mercaptide polysulfides.

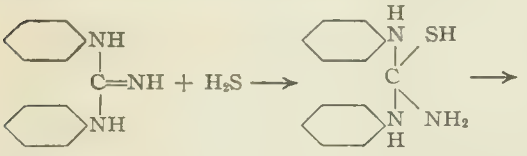
The action of thiocarbanilide to produce phenyl mustard oil and this to produce mercaptobenzothiazole, according to Bruni, is believed to be inoperative except as carried on by sulfur reaction prior to compounding the accelerator. Phenyl mustard oil in a zinc-sulfur-rubber mix is inactive as an accelerator and Bruni's reactions do not take place.

Reactions of Guanidines

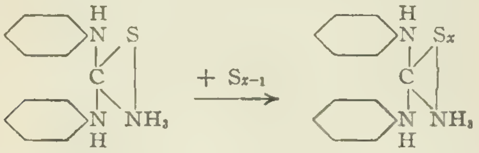
Kratz, Flower and Coolidge[26] have shown the higher curing power of mono- and diphenylguanidine as compared with the triphenyl derivative. The present writers have found some very interesting reactions of the guanidines which take place during the vulcanizing process through the action of hydrogen sulfide and sulfur, and which aid in explaining their relative curing powers as well as their mechanism of vulcanization.

1—With sulfur in benzene at room temperature, triphenylguanidine becomes light red in color if subjected to the action of hydrogen sulfide.

2—Under the same conditions diphenylguanidine gives a much deeper red color. This action is explained by the formation of a peculiar derivative of ammonium sulfide which readily forms polysulfides.



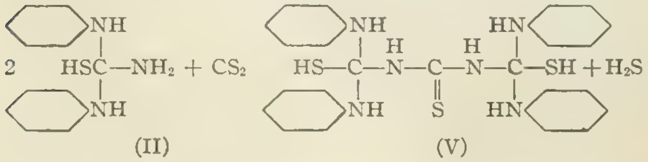
(I) (II)



(III) (IV)

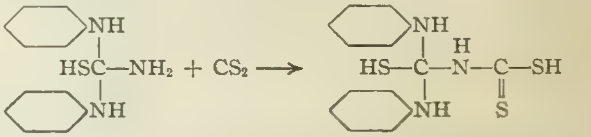
Form III may be considered as a derivative of ammonium sulfide.

3—The free amino group of Form II is further proved by its reaction with carbon disulfide. A substituted thiourea is formed and the total weight of the reaction product corresponds to the following equation:



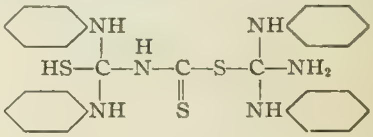
(II) (V)

4—Further evidence of these reactions is found by passing hydrogen sulfide into a carbon disulfide solution of diphenylguanidine. The first few bubbles of the gas cause a complete precipitation of the guanidine as a resin. The colloidal character of this resin indicates a high molecular weight. Further action of the gas causes no change. We attribute this phenomenon to the action of the dithiocarbamate as being similar to that of hydrogen sulfide through the carbosulfhydryl group. The first trace of the gas gives a small amount of Form II, which forms a dithiocarbamate with carbon disulfide.



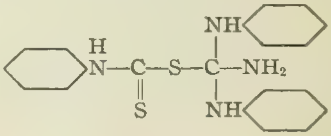
(II) (VI)

This dithiocarbamate then reacts with a second mole of the guanidine to give Form VII.



(VII)

Form VII is an amine and therefore reacts further with carbon disulfide, and the process is repeated until a high molecular weight is built up and a resin formed.



(VIII)

5—One mole each of aniline, carbon disulfide, and diphenylguanidine will form an additive compound, on mixing in solution, whose total dry weight corresponds to Formula VIII. This product will react with more carbon disulfide through the amino group.

6—Mercaptans also form additive products with diphenylguanidine and form red polysulfides with sulfur in solution.

7—Metallic hydrosulfides, ammonium hydrosulfide, metallic hydrates and oxides give characteristic reactions with the guanidine or Form II.

In all of the above reactions triphenylguanidine is less reactive and in some cases the products are unstable or do not form. The above polysulfides of the guanidines are similar to those of ammonium sulfide and do not cure cements at room temperature. In heat cures diphenylguanidine is more reactive than is triphenylguanidine. The effect of zinc oxide on diphenylguanidine and its curing power is rather peculiar. In many cases the time of cure is not changed by the zinc oxide, while in others it is materially retarded. Kratz has noted the retarding action of zinc oxide on aniline. We have found three classes of organic accelerators based on the effect of metallic oxides. There are accelerators which are aided or retarded by the action of zinc, while there are others which seem to be unaffected.

The above data do not preclude the decomposition of Form III into ammonia and thiocarbanilide in high temperature cures with the corresponding reactions whereby they activate sulfur.

The inactivity of zinc oxide on the curing time of this guanidine at 40 lbs.' steam pressure indicates that this reaction does not take place at this temperature during vulcanization.

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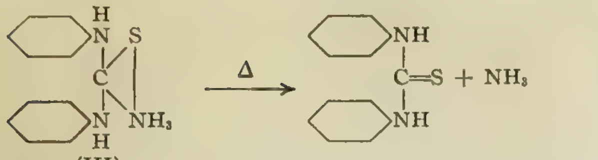
[26] This Journal, 12 (1920), 319.



(III)

SUMMARY ON GUANIDINES—Guanidine accelerators form derivatives of ammonium sulfide by reaction with hydrogen sulfide even at ordinary temperatures. Polysulfides easily form and the aid of metallic oxides is not required except as inorganic fillers. In some cases the action of zinc oxide is that of a retardant. Further research is desirable.

INORGANIC POLYSULFIDES

Schiff[27] studied the polysulfides of a large number of heavy metals other than those of antimony and arsenic. He found most of them to be unstable and obtainable only under special conditions and for a short time, but he stated that the polysulfides of zinc and cadmium do not easily decompose, and can be isolated and manipulated.

In repeating the work of Schiff, the writers have observed the following phenomena: With dilute solutions of zinc salts and sodium pentasulfide a large portion of the zinc solution, preferably the acetate, may be added to the dilute polysulfide solution without causing a precipitate to form. This reaction is similar to the one pointed out by Thomsen.[28]

$$Zn(OAc)_2 + 2Na_2S \longrightarrow 2NaOAc + Zn(S{-}Na)_2 \quad \underline{\text{Soluble}}$$
$$Zn(OAc)_2 + 2Na_2S_5 \longrightarrow 2NaOAc + Zn(S_5{-}Na)_2 \quad \underline{\text{Soluble}}$$

Upon further addition of the zinc solution there is formed a precipitate which is colloidal in character and passes through filter paper. The high molecular weight of similar precipitates has been shown by Linder and Picton.[29] We therefore write the next step in the reaction as follows:

$$2Zn(S_5{-}Na)_2 + Zn(OAc)_2 \longrightarrow 2NaOAc + Zn(S_5{-}Zn{-}S_5Na)_2$$

Upon continuing the addition of the zinc solution up to molar proportions or excess, the precipitate granulates and may be filtered. This precipitate, therefore, consists of $(ZnS_5)_x$ whose formula may be represented as $AcOZn{-}S_5(Zn{-}S_5)_xZn{-}OAc$, or without the final acetate groups if the chain of $-Zn-S_5-$ links be closed. Upon filtering this precipitate, the filtrate is clear, and there is no evidence of colloidal free sulfur. Schiff states that it may be washed with hot water without decomposing the pentasulfide.

The writers have compounded this zinc pentasulfide with rubber, preferably using it as a slightly damp paste and later drying, and have found it a strong curing agent. Figuring four of the sulfurs as available for vulcanization and compounding for 5 per cent of available sulfur on the rubber, they obtained a well-set cure in 45 min., a full cure in from 75 to 90 min., and a distinct overcure in 2 hrs. All cures were at the temperature of 40 lbs. of steam. Five per cent of ordinary sulfur would not give a satisfactory cure in less than 3.5 hrs.

The question of reversibility of the equation $ZnS_5 = ZnS + S_4$ was investigated, in consideration of the fact that rubber cured with the pentasulfide of zinc shows the well-known "sulfuring up" or "bloom." Freshly precipitated zinc sulfide containing no extra sulfur was compounded with sulfur to duplicate the above formula containing 5 per cent sulfur on the rubber. The rapidity of vulcanization was similar to that with pentasulfide, but with lower tensiles. In no case did the sulfide contain free alkali. We find, therefore, that inorganic zinc-sulfur compounds easily form polysulfides which contain active sulfur available for vulcanization purposes, which is far more active than elemental sulfur.

In conclusion the writers wish to call attention to the complicated reactions which attend the vulcanization process by the use of each individual accelerator. In nearly every instance there are two or more mechanisms for the formation of active sulfur and it is as yet impossible to state which reaction predominates. The additional use of inorganic acids further complicates the subject and mixed organic accelerators furnish additional complexity. Further research on each individual accelerator is needed.

The authors believe that they have established the fundamental principles for the science of vulcanization of rubber by sulfur. A few blocks may have been misplaced, but the corner stones seem to be truly set. They are pleased that Prof. Bruni has corroborated their findings and have no desire for a priority polemic.

SUMMARY

1—There is described a new form of sulfur which will vulcanize rubber at low temperatures without the aid of accelerators. This sulfur is believed to be trithio-ozone.

2—Zinc persulfides are shown to be active vulcanization agents and zinc sulfide to be an accelerator when properly prepared. Methods for preparing these active compounds are given.

3—Zinc mercaptides, as well as the mercaptides of other metals, form persulfides without the formation of inorganic sulfides. These mercaptide polysulfides furnish the most active sulfur of all accelerators known to-day. Dithiocarbamates are classed as mercaptides.

4—Thiocarbanilide functions as a mercaptan. Its zinc and lead mercaptides have been described.

5—Basic or mixed mercaptides of polyvalent metals are described which have regular organic mercaptide groups on one side of the metal with sulfhydryl, hydroxy, acidic or other groupings on the other side.

6—The polysulfide of lead mercaptobenzothiazole has been described as a red compound which vulcanizes rubber at ordinary temperatures.

7—New reactions and data on the guanidine accelerators are given. They are classed as "hydrogen sulfide polysulfide accelerators."

8—Nitroso accelerators are reserved for future discussion.

9—Organic disulfides and their polysulfides are shown to be less active curing agents than the corresponding mercaptans or their zinc salts.

10—Further research is needed on vulcanization reactions in the absence of inorganic accelerators, especially for the mechanism of vulcanization by aniline and sulfur.

11—Hydrogen sulfide is shown to be an important factor in the mechanism of vulcanization by many accelerators.

12—All vulcanizing reactions are described as due to some form of polysulfide sulfur. Trithio-ozone, as well as metallic, organo-metallic and organic polysulfides, furnishes sulfur in a more active state than elementary sulfur.

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[27] *Loc. cit.*

[28] *Ber.*, **11** (1878), 2044.

[29] *J. Chem. Soc.*, **61** (1892), 114.

Lectures at Philadelphia College of Pharmacy and Science

Somewhat in line with President Smith's advocacy of popular lectures on chemical subjects, referred to in our November editorials, is the free public lecture course which is being given at the Philadelphia College of Pharmacy and Science. The subjects include:

The Chemistry of Other Worlds
Petroleum and Its Products and Their Modern Uses
Products from Cotton Fields and Forests
Strawberries at the North Pole and Apples at the Equator
Our Bacterial Friends and Enemies
Chemistry in Peace and War
A Thousand and One Odors
Standardized Remedies
How Chemistry Develops the Industries
One Drop of Blood
The Foods of the Next Century
The Raw Materials of the Chemical Industry
Food from the Air
Natural Silk and Artificial Silk

The Swelling and Gelation of Gelatin[1]

By **Robert H. Bogue**

Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

In several papers by Martin Fischer and his collaborators[2] it has been shown that the tendency of gelatin to go into solution in mixtures of the salts of polybasic acids increases progressively as the amount of acid or alkali in these mixtures is increased from a given low point. They find further that the highest degree of swelling is obtained in the pure acid solution, that this decreases to a minimum in a solution consisting essentially, for example, of monosodium phosphate, and that the swelling again increases on the alkaline side of this point through the di- and the trisodium phosphates to the pure alkali, at which point it is nearly as high as in the pure acid. In other words, gelatin swells the least, and is not liquefied, in a solution of monosodium phosphate, a solution of about equal parts of monosodium and disodium citrate, and a solution of pure sodium bicarbonate. As the solutions become either more acid or more alkaline the swelling is increased, and they tend ever more strongly to liquefy.

It would seem that the above effects were controlled by the hydrogen-ion concentration of the solution. Patten and Johnson,[3] in repeating a part of the work of Fischer and his collaborators, have shown that the region of least swelling and of least tendency to go into solution corresponds with a pH value of from 4.4 to 5.7. These values correspond reasonably well with the findings of Loeb[4] that the minimum degree of swelling, viscosity, osmotic pressure, alcohol number, and conductivity all fall very close to, or directly at, the isoelectric point, which is for gelatin pH = 4.7.

Another conception which has long been given credence to account for the causes of the alteration in the properties of gelatin under the influence of electrolytes is that the size of the charge on the cation or the anion is the dominant influence. The experiments of Fischer are nonconclusive in this respect, although Fischer himself refers to the changes as being brought about by *acids* and *alkalies*. He avoids a consideration, however, of hydrogen-ion concentration as distinguished from what is generally referred to as acidity or alkalinity.

In connection with some work upon the effect of silicates of sodium on the properties of gelatin, the writer has obtained data which seem to indicate that the variation in hydrogen-ion concentration and the valency of the combined ions may be adequate to account for all variations in properties which are observed.

EXPERIMENTAL

The silicates of sodium[5] which were used consisted of seven of varying composition as follows:

TABLE I—COMPOSITION OF SILICATES OF SODIUM

No.	Per cent Na_2O	Per cent SiO_2	Per cent H_2O	Approximate Molecular Structure
1	7.0	26.9	66.1	$Na_2O.4SiO_2.33H_2O$
2	8.98	30.3	60.72	$Na_2O.3.5SiO_2.23H_2O$
3	11.0	31.2	57.8	$Na_2O.3SiO_2.18H_2O$
4	13.7	32.9	53.4	$Na_2O.2.5SiO_2.13H_2O$
5	17.83	36.45	45.72	$Na_2O.2SiO_2.9H_2O$
6	24.2	38.3	37.5	$Na_2O.1.5SiO_2.5H_2O$
7	26.95	28.85	44.2	$Na_2O.SiO_2.6H_2O$

These silicates were made up into two series, one containing 2 per cent of Na_2O throughout, with consequently varying amounts of SiO_2, and the other containing 4 per cent of SiO_2 throughout, with varying amounts of Na_2O. It has previously been shown[6] that solutions of the silicates of sodium which contain equal amounts of Na_2O by weight, but varying amounts of SiO_2, do not possess the same concentration of hydroxyl ion, but that the latter increases as the ratio of soda to silica in the molecule increases.

The make-up of the two series, together with their pH values, is shown in Table II.

TABLE II—COMPOSITION OF SILICATE SERIES

NUMBER	Per cent Na_2O	Per cent SiO_2	pH (0.01*M*)
		Series 1	
1	2.0	7.7	10.80
2	2.0	6.7	10.90
3	2.0	5.7	11.08
4	2.0	4.8	11.16
5	2.0	4.1	11.50
6	2.0	3.2	11.95
7	2.0	2.1	12.43
8	2.0	0.0	13.57
		Series 2	
1	1.1	4.0	10.68
2	1.2	4.0	10.79
3	1.4	4.0	10.98
4	1.7	4.0	11.11
5	2.0	4.0	11.50
6	2.5	4.0	12.08
7	3.7	4.0	12.62

In the first experiment small portions of the silicates were added in successive stages to the sol of a high-grade gelatin of such concentration that the final product contained always 3 per cent of gelatin. The relative consistency only was measured. The results are tabulated in Tables III and IV.

TABLE III—EFFECT OF SILICATE SERIES 1 ON LIQUEFACTION OF GELATIN
(5 cc. 6 per cent gelatin + 4 cc. water = *a*)

NUMBER	COMPOSITION OF MIXTURE	STATE
1	*a* + 1.0 cc. water (control).	Solid
2	*a* + 0.5 cc. water + 0.5 cc. Silicate 1	Solid
3	*a* + 1.0 cc. Silicate 1	Solid
4	*a* + 0.5 cc. Silicate 1 + 0.5 cc. Silicate 2	Solid
5	*a* + 1.0 cc. Silicate 2	Solid
6	*a* + 0.5 cc. Silicate 2 + 0.5 cc. Silicate 3	Solid
7	*a* + 1.0 cc. Silicate 3	Solid
8	*a* + 0.5 cc. Silicate 3 + 0.5 cc. Silicate 4	Solid
9	*a* + 1.0 cc. Silicate 4	Solid
10	*a* + 0.5 cc. Silicate 4 + 0.5 cc. Silicate 5	Solid
11	*a* + 1.0 cc. Silicate 5	Solid
12	*a* + 0.5 cc. Silicate 5 + 0.5 cc. Silicate 6	Semisolid
13	*a* + 1.0 cc. Silicate 6	Semisolid
14	*a* + 0.5 cc. Silicate 6 + 0.5 cc. Silicate 7	Semisolid
15	*a* + 1.0 cc. Silicate 7	Liquid
16	*a* + 0.5 cc. Silicate 7 + 0.5 cc. Sodium hydroxide 8	Liquid
17	*a* + 1.0 cc. Sodium Hydroxide 8	Liquid

TABLE IV—EFFECT OF SILICATE SERIES 2 ON LIQUEFACTION OF GELATIN
(5 cc. 6 per cent gelatin + 4 cc. water = *a*)

NUMBER	COMPOSITION OF MIXTURE	STATE
1	*a* + 1.0 cc. water (control)	Solid
2	*a* + 0.5 cc. water + 0.5 cc. Silicate 1	Solid
3	*a* + 1.0 cc. Silicate 1	Solid
4	*a* + 0.5 cc. Silicate 1 + 0.5 cc. Silicate 2	Solid
5	*a* + 1.0 cc. Silicate 2	Solid
6	*a* + 0.5 cc. Silicate 2 + 0.5 cc. Silicate 3	Solid
7	*a* + 1.0 cc. Silicate 3	Solid
8	*a* + 0.5 cc. Silicate 3 + 0.5 cc. Silicate 4	Solid
9	*a* + 1.0 cc. Silicate 4	Solid
10	*a* + 0.5 cc. Silicate 4 + 0.5 cc. Silicate 5	Semisolid
11	*a* + 1.0 cc. Silicate 5	Semisolid
12	*a* + 0.5 cc. Silicate 5 + 0.5 cc. Silicate 6	Liquid
13	*a* + 1.0 cc. Silicate 6	Liquid
14	*a* + 0.5 cc. Silicate 6 + 0.5 cc. Silicate 7	Liquid
15	*a* + 1.0 cc. Silicate 7	Liquid

IMPROVED PROCEDURE—In order that more comprehensive data might be obtained a more elaborate procedure was adopted. Cylindrical glass funnels about 25 mm. in diameter and 80 mm. in height were fitted with filter paper, and the outlet tubes were closed by a short sealed piece of rubber tubing. Into these was introduced an excess of the several silicate solutions described, the temperature being about

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Fischer, Hooker, Benzinger, and Coffman, *Science*, N. S., **46** (1917), 189; Fischer and Hooker, *J. Am. Chem. Soc.*, **40** (1918), 272; Fischer and Coffman, *Ibid.*, **40** (1919), 303.

[3] *J. Biol. Chem.*, **38** (1919), 179.

[4] *J. Gen. Physiol.*, **1** (1918–19), 39, 237, 363, 483, 559.

[5] The author is indebted to the Philadelphia Quartz Co. for the silicates experimented upon. The analyses of these samples were furnished by William Stericker (Mellon Institute).

[6] R. H. Bogue, *J. Am. Chem. Soc.*, **42** (1920), 2575.

10° C. One-gram portions of the gelatin which had been ground so as to pass a 40-mesh, but retained by a 60-mesh, sieve were poured into each funnel and stirred. After an hour the excess of liquid was drawn off, the gelatin washed by several perfusions of distilled water, and the swelling measured directly in millimeters to which the gelatin rose in the tube. The gelatin was then transferred to small beakers, water was added, and the gelatin brought into solution by warming. Each sample was made up to 100 cc., *e. g.*, a 1 per cent solution, and the viscosity, alcohol number, jelly consistency, and hydrogen-ion concentration were determined.

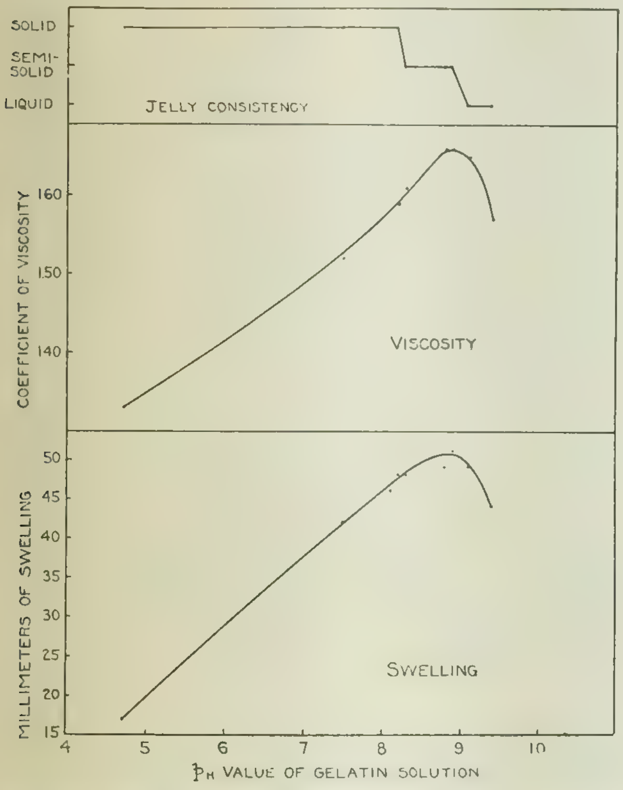

FIG. 1—THE JELLY CONSISTENCY, VISCOSITY, AND SWELLING OF GELATIN AT VARYING pH VALUES. (TABLE VI, SERIES 1)

Viscosity—The viscosity was measured by an Ostwald viscosimeter immersed in a water thermostat set at 35° C. This temperature was selected for the viscosity measurements in order that no complications due to an equilibrium between what C. R. Smith[7] calls the sol form A and gel form B might arise. At 35° the sol form only can exist. The figures given are obtained by dividing the time in seconds for the outflow of the gelatin by the corresponding time for water at the same temperature.

Alcohol number—The alcohol number is taken as the number of cubic centimeters of 95 per cent alcohol which are required to precipitate or produce a definite turbidity in 5 cc. of the gelatin sol at 30° C.

Jelly consistency—The jelly consistency was noted by allowing 10 cc. of the gelatin-silicate mixtures to stand for 12 hrs. at 10° C. Only three degrees of consistency were observed: solid, semisolid, and liquid.

H-ion concentration—The hydrogen-ion concentration was determined by electrometric means. The hydrogen cell was of the type suggested by Clark.[8] Tenth-normal calomel cells, which were made up with great care, were employed. The hydrogen was supplied from a commercial tank and purified by passing through alkaline permanganate, concentrated sulfuric acid, and water containing a little barium chloride. The gas chain and the hydrogen purifying chain were enclosed in an air thermostat set at 30° C. The average deviation during measurements was not greater than ±0.02°. The measurements were made by the use of a Leeds and Northrup type K potentiometer. The value of pH was calculated from the electrode potential by the equation

$$\mathrm{pH} = \frac{E - 0.337}{0.0601},$$

which was derived from the well-known formula of Nernst:

$$E = E_o + \frac{RT}{nF} \log_e C,$$

where pH is the log of 1/hydrogen-ion concentration, E the electrode potential at concentration C, E*o* the electrode potential at molar concentration, R the gas constant, T the absolute temperature, *n* the valency of the ion, F the Faraday constant, and C the ionic concentration of the solution.

TESTS ON NORMAL GELATIN—The data obtained by using the gelatin in the normal condition are shown in Table V.

TABLE V—EFFECT OF SILICATES ON PROPERTIES OF NORMAL GELATIN

No.	Per cent Na_2O	Per cent SiO_2	Swelling	Coefficient of Viscosity	Alcohol Number	Jelly Consistency	pH
				Series 1			
0	0.0	0.0	20	1.41	8	Solid	5.8
1	2.0	7.7	37	1.49	23	Solid	7.9
2	2.0	6.7	40	1.51	25	Solid	8.5
3	2.0	5.7	45	1.53	25	Semisolid	8.6
4	2.0	4.8	47	1.58	26	Semisolid	8.7
5	2.0	4.1	47	1.61	25	Semisolid	9.1
6	2.0	3.2	44	1.57	26	Liquid	9.5
7	2.0	2.1	44	1.55	27	Liquid	9.6
8	2.0	0.0	43	1.48	29	Liquid	9.9
				Series 2			
0	0.0	0.0	20	1.41	8	Solid	5.8
1	1.1	4.0	34	1.48	20	Solid	7.5
2	1.2	4.0	38	1.50	22	Solid	7.9
3	1.4	4.0	42	1.52	24	Solid	8.2
4	1.7	4.0	45	1.58	25	Semisolid	8.4
5	2.0	4.0	47	1.61	25	Semisolid	9.1
6	2.5	4.0	46	1.59	27	Liquid	10.0
7	3.7	4.0	43	1.49	30	Liquid	10.8

TESTS ON ISOELECTRIC GELATIN—The above experiments were repeated, but instead of the gelatin in its normal condition, which was essentially calcium gelatinate of a pH of 5.8, the gelatin used was first rendered isoelectric by allowing it to soak for an hour in *N*/128 hydrochloric acid and filtering and washing out the excess of acid by several perfusions with distilled water. The pH value of a 1 per cent solution was found to be 4.7, which is the value of gelatin at its isoelectric point. The data are shown in Table VI.

TABLE VI—EFFECT OF SILICATES ON PROPERTIES OF ISOELECTRIC GELATIN

No.	Per cent Na_2O	Per cent SiO_2	Swelling	Coefficient of Viscosity	Alcohol Number	Jelly Consistency	pH
				Series 1			
0	0.0	0.0	17	1.33	4	Solid	4.7
1	2.0	7.7	42	1.52	24	Solid	7.5
2	2.0	6.7	46	1.58	25	Solid	8.1
3	2.0	5.7	48	1.59	25	Solid	8.2
4	2.0	4.8	48	1.61	26	Semisolid	8.3
5	2.0	4.1	49	1.66	25	Semisolid	8.8
6	2.0	3.2	51	1.66	26	Semisolid	8.9
7	2.0	2.1	49	1.65	30	Liquid	9.1
8	2.0	0.0	44	1.57	32	Liquid	9.4
				Series 2			
0	0.0	0.0	17	1.33	4	Solid	4.7
1	1.1	4.0	39	1.47	23	Solid	7.1
2	1.2	4.0	41	1.49	24	Solid	7.5
3	1.4	4.0	44	1.56	24	Solid	7.8
4	1.7	4.0	46	1.58	25	Solid	8.1
5	2.0	4.0	49	1.66	25	Semisolid	8.7
6	2.5	4.0	48	1.64	30	Semisolid	9.6
7	3.7	4.0	46	1.59	35	Liquid	10.4

In Fig. 1, the jelly consistency, viscosity, and swelling of Series 1 in Table VI are plotted against the pH values.

DISCUSSION

An inspection of the data presented in the several tables and in the figure brings out many points that are of interest. The swelling is found to progress regularly in Series 1 with decreasing silica content, the percentage of soda present being held constant, and in Series 2 with increasing soda content, the silica in this case being kept constant. This increase in swelling does not continue throughout the entire extent of the series, however, but reaches a maximum beyond which it drops slightly. The coefficient of viscosity is found to behave in an entirely similar manner, as would be expected from the findings previously reported[9] which have shown that solution and viscosity are parallel functions, and swelling is a measure of solvation. If the hydrogen-ion concentration were not simultaneously determined it would be assumed that, in Series 1, the variation in swelling and viscosity were directly attributable to the regular variation in the percentage of silica present, since the soda content remains constant.

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[7] *J. Am. Chem. Soc.*, **41** (1919), 135; THIS JOURNAL, **12** (1920), 878.

[8] *J. Biol. Chem.*, **23** (1915), 475.

But the pH values are found to increase regularly also, and this increase cannot conceivably be attributed to the decrease in silica content *per se*, because the silicic acids have many times been shown to be un-ionized. The only conclusion which may be drawn to account for the increase in the pH value is that as the content of silicic acid in the molecule of the sodium silicates decreases the sodium hydroxide actually present in an ionized condition increases. And this in turn may be brought about only by a continually increasing degree of hydrolysis of the silicates with increasing ratio $Na_2O:SiO_2$. Furthermore, the differences in degree of hydrolytic dissociation on passing through the silicate series must be considerable in order to account for the wide variation in pH, *e. g.*, in Table VI, Series 2, from No. 1 (pH = 7.1) to No. 7 (pH = 10.4). These results are in complete accord with, and therefore tend to confirm, the conclusions reported in an earlier paper,[10] to the effect that the hydrolysis of the silicates of sodium increases as the ratio of Na_2O to SiO_2 in the molecule increases.

The alcohol number is found to rise regularly with increasing pH, and might conceivably be utilized for the purpose of roughly locating the hydrogen-ion concentration of a solution of gelatin.

The jelly consistency is solid at the lower pH values, but in the neighborhood of pH = 8.5 a softening is observed, while at a pH of about 9.5 the gelatin will no longer gel at 10°. The relation of the jelly consistency to the swelling and the viscosity should be especially observed. At the point where the maximum swelling and viscosity are attained the jelly is no longer firm, but has become soft. This is well illustrated in Fig. 1. On further increases in pH, swelling and viscosity begin to decline, and the gelatin, at the concentration used, remains liquid.

This has an important bearing on the explanation of the mechanism of gelation. As the gelatin is brought into the presence of increasing quantities of sodium hyroxide, constantly increasing amounts of gelatin will, according to Loeb[4] be converted into sodium gelatinate. This gelatinate is shown to possess a strong tendency towards solvation, *e. g.*, it swells to a considerable extent. But it also is much more soluble, according to Loeb, than gelatin *per se* and so will not gel under the conditions of our experiment.

But may gelation, and precipitation or coagulation, be regarded as identical? In other words, is gelation dependent primarily upon solubility? There is no doubt that gelatin at its isoelectric point is actually much less soluble than under any other electrical condition. A white, almost granular, precipitate may be obtained by bringing gelatin to that condition. But the writer has data which show that the consistency of the jelly under those conditions may actually be less than at slight intervals on either side of that point. Gelation appears rather to be due to an increase in the solvation or *hydration* of the dispersed particles while true precipitation and coagulation take place only under conditions of excessive *dehydration*. That solvation and viscosity run parallel has already been shown,[9] and the fact that the viscosity at 30° begins to drop when the liquid at 10° will no longer solidify is significant. Swelling is known to be increased by low temperatures, and viscosity is also increased by low temperatures. Gelation is similarly influenced, which means that solvation is much greater at low than at high temperatures. All of our data confirm this point of view.

Since the volume occupied by the dispersed phase is very nearly defined by the degree of solvation, the size of the molecule, *e. g.*, the volume occupied by unit weight of dispersed phase, will be the determining factor in both the degree of swelling, the viscosity, and the jelly consistency of the gelatin. This statement must not be construed to mean, however, that the greater the volume per unit weight of gelatin the greater also will be the value of each of the above properties indefinitely. If this volume is very small, then the three properties under discussion will also be small; if this volume be very large then, it being mostly water, the consistency and viscosity will again be small, and as the conditions which make for increased size also make for increased solubility (*e. g.*, gelatin chloride and sodium gelatinate are more soluble than gelatin) a point must be eventually reached beyond which further additions of acid or alkali will result more in favor of solution than of increased size from hydration. But at intermediate values the degree of each of these properties reaches its maximum.

The effect of the silicates upon the properties of the isoelectric gelatin is quite similar to that observed in the normal gelatin (calcium gelatinate). The swelling and viscosity are somewhat higher in the isoelectric series, but this is probably due, as Loeb has found in similar cases, to the fact that calcium gelatinate exhibits a lower degree of swelling and viscosity than sodium gelatinate, and that the presence of the divalent calcium ion retards the greater activity of the monovalent sodium ion in this respect. By rendering the gelatin isoelectric and washing it as described, the calcium ion is largely removed.

SUMMARY

Experiments have been conducted upon gelatin sols and gels that have been treated with silicates of sodium in which the ratio of Na_2O to SiO_2 in the molecule varied regularly from 1:4 to 1:1. The solutions were made up so that the actual amount of Na_2O was constant in one series, while the actual amount of SiO_2 was constant in the other series. The degree of swelling, viscosity, alcohol number, and pH value were determined in each series, both upon the normal gelatin, which was essentially calcium gelatinate of a pH of 5.8, and upon the gelatin which had been rendered isoelectric and had a pH value of 4.7.

The data obtained show that the swelling and the viscosity increase, in Series 1, with a decrease in the silica content, the percentage of soda being held constant. The pH value is shown to increase constantly, however, as the ratio $Na_2O:SiO_2$ increases. This is due to an increase in the degree of hydrolysis of the silicates. The variation in the above-mentioned properties appears to be dependent upon the pH value, rather than upon the changing silica content. This is further evidenced by the similar behavior of Series 2, in which the silica content remains constant.

The swelling and viscosity reach their maximum value at a pH of about 8.5, and decrease slightly at higher values. The jelly consistency, however, is solid at pH values between 4.7 and 8.0, but at 8.5 it becomes soft, and liquefies at 9.0 and above. This affords the basis of an argument which concludes that gelation is due to and dependent upon the tendency of the substance to become solvated, the volume occupied by unit weight of dispersed phase being the determining factor. When this volume is very small or very

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[9] R. H. Bogue, *J. Am. Chem. Soc.*, **43** (1921), 1764.

[10] *Ibid.*, **42** (1920), 2575.

large the jelly consistency will be small, and, at intermediate values of volume per unit weight, the jelly consistency will reach its maximum.

The results upon isoelectric gelatin are similar to those obtained with normal gelatin, except that higher degrees of swelling and viscosity are attained, because of the absence of the retarding divalent calcium ion.

The alcohol number is found to rise regularly with increasing pH, and it is suggested that this value may be utilized for rough measurements of pH.

The Chemical Changes Involved during Infection and Decay of Wood and Wood Pulp[1]

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A knowledge of the chemical composition of woods and pulps, linked with a study of the changes in composition after infection[2] with specific organisms of molds and wood-destroyers, is of considerable importance in that it throws further light on the astonishing losses sustained through the decay of wood and pulp and in the pulping and conversion into paper of such infected wood and pulp.

A mere study of the organisms of decay, without a thorough investigation of the chemical changes involved, would help but little in solving the problem, because an infected log or lap of pulp may look more or less sound and yet contain wood-destroying fungi which have chemically changed the cellulose, rendering it very much less resistant. By the study of the chemical changes involved, the progress of decay may easily be followed, and the cause of the large losses in pulping infected woods may also be explained.

The methods of analysis, with the exception of the determinations of lignin,[3] solubility in 7.14 per cent sodium hydroxide[4] (α-, β-, and γ-celluloses),[5] and copper number[6] were those described by A. W. Schorger[7] in the "Analysis of Some American Woods." The methods used were chosen with the purpose of following the progress of decay of wood and pulps, and of obtaining data, if possible, which would aid in ascertaining the chemical changes which these substances undergo during decay. It was also hoped to explain the effects of decay on the yield, quality, and pulping characteristics of wood by the mechanical, sulfite, and soda processes.

The cellulose content of the woods and pulps is undoubtedly the constant of most vital importance in the manufacture of paper. This value was therefore determined directly by the Cross and Bevan method, and the nature and progress of decomposition of the cellulose derived from sound and decayed material were studied. Data regarding the latter were obtained by determining the resistance toward chemical reagents, such as the copper number, and the percentages of α-, β-, and γ-celluloses.

The percentage of lignin or noncellulose materials is of importance in the manufacture of chemical pulp; therefore a knowledge of its rate of decomposition relative to that of cellulose would determine whether or not the organisms of decay produced a uniform degradation or selective action on woods and pulps.

The comparison of the solubility in hot and cold water of the sound and decayed woods and pulps would be a direct measure of the losses sustained through the use of decayed materials. These constants would also indicate the extent of decay, as Rose and Lisse have pointed out that decay is associated with increasing molecular simplicity.

During decay wood breaks down to a considerable extent into substances which are almost entirely soluble in alkali.[2] The solubility of the sound and decayed woods and pulps in strong (7.14 per cent NaOH) and weak (1 per cent NaOH) alkali would be a measure of the progress of decay and also show the hydrolytic action of the organisms of decay. This value would also tend to explain the results obtained in pulping decayed woods by the soda process.

Since the reducing properties of wood and pulp are increased during decay, due partly to the increase in the percentage of the less stable or less resistant celluloses, *viz.*, β- and γ-, and other substances, the copper number was determined. It also seemed desirable to show the relation between the ether-soluble content, the ash, the pentosan, and methylpentosan contents of sound and decayed woods and pulps. The moisture content was determined in order to make the calculations of all results for comparative purposes on the oven-dry (105° C.) or moisture-free basis.

Through the courtesy of a large number of mills cooperating with the Forest Products Laboratory, a number of shipments of sound and infected woods and pulps were received for chemical and pulping studies and for isolation of the typical organisms causing the decay.

The woods studied were spruce, balsam, hemlock, and aspen, representing various stages of decay, determined microscopically.

COMPARISON OF SOUND AND INFECTED SPRUCE WOODS AND PULPS DERIVED FROM THEM BY MECHANICAL, SULFITE, AND SODA PROCESSES

The sample of fresh sound spruce wood used as a standard of comparison was obtained from the Marathon Paper Mills Co., Rothschild, Wis. The infected spruce woods, representing various stages of decay, as determined by the eye, were carefully selected from the following sources:

1—Very slightly infected, containing some mycelium (determined microscopically), from Cloquet, Minn.

2—Slightly infected, taken from the top of a pile of logs at the Marathon Paper Mills Co., Rothschild, Wis.

3—Wood considerably more infected, taken from the bottom of a pile of logs at the Marathon Paper Mills Co.

4—Very badly infected wood, such as would be rejected for pulping purposes, obtained from the Wausau Paper Mills Co., Brokaw, Wis.

Samples of these woods were shipped to the Forest Products Laboratory for chemical analysis and pulping trials, while some of the wood was made into mechanical pulps on experimental mill runs. The results of the pulping trials will be given in a later publication.[8]

In order to establish the percentage of cellulose as a standard for comparison, and the relation of this constituent to

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[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26–29, 1921.

[2] It has been shown by Rose and Lisse that wood undergoes a chemical change during decay. THIS JOURNAL, **9** (1917), 284.

[3] Ost and Wilkening, *Chem.-Ztg.*, **461** (1910); Cross and Bevan, "Researches on Cellulose," **III** (1905–10), 39.

[4] Ordnance Department, U. S. A., *Pamphlet* **450** (1918), 16.

[5] Cross and Bevan, "Paper Making," **1916**, 97; Schwalbe, "Chemie der Cellulose," **1911**, 637.

[6] Schwalbe, *Ibid.*, 625.

[7] THIS JOURNAL, **9** (1917), 556.

[8] Otto Kress, C. J. Humphrey, C. A. Richards, M. W. Bray, and J. A. Staidl, "Deterioration of Wood Pulp and Pulpwood."

TABLE I—RESULTS[1] OF THE CHEMICAL ANALYSES OF SAMPLES OF SOUND (WHITE SPRUCE) WOOD FROM VARIOUS PARTS OF NORTH AMERICA

No.	Company; Location; Location Where Wood Was Grown; Remarks	Moisture	Lignin	Cellulose	Ether-Soluble	Alcohol-Soluble	Annual Rings	Results of Microscopic Analysis
....	Sound white spruce (Schorger) from Mellon, Wis.	...	...	61.85	1.36	..	..	Reported as sound
2549	Sound white spruce, Cloquet, Minn.	12.18	30.60	54.65	1.58	..	..	......
I*d* & *g*	Pejepscot from cut 10 mi. north of Brunswick, Me.	4.26	26.85	59.70	0.69	0.82	18	Sound
II-A	Northern Paper Mills, Green Bay, Wis. Cl. white spruce	5.02	29.50	57.50	0.15	1.71	53	Considerable mycelium
III-A & *bx*	Fletcher Paper Co., Alpena, Mich.	4.24	27.90	58.10	0.96	1.07	27	An occasional thread of mycelium
IV-A	S. D. Warren Co., Cumberland Mills, Me.	4.48	26.93	60.15	0.64	0.84	75	Sound
V-A	Marathon Paper Mills, Rothschild, Wis. Fresh sound Wisconsin spruce	3.17	28.30	58.58	1.24	0.83	80	Sound
VI-A	Groveton Paper Mills Co., Groveton, N. H. Spruce woods	5.02	28.12	60.75	0.86	1.10	47	Sound
VII-C	Port Huron Sulphite & Paper Co., Port Huron, Mich. White spruce from Edmunton, Alberta, Canada	3.38	26.89	61.70	0.72	0.41	64	Occasional thread of mycelium
VIII-B	Riordon Co., Ltd., Hawkesbury, Ont.	4.51	28.00	61.10	0.71	1.07	110	Occasional thread of mycelium
IX-A	Hammermill Paper Co., Erie, Pa. White spruce from Ft. William, Canada	3.62	27.60	59.30	0.71	1.17	85	Sound
XB	Laurentide Co., Ltd., Grand Mere, Que., Canada. White spruce from this region	4.98	28.10	60.55	1.53	0.95	40	Sound
XI-A	Abitibi Pulp & Paper Co., Iroquois Falls, Ont. Secured from the bush	5.60	28.41	57.35	1.79	1.56	48	......
XIII-B	Price Bros. Co., Ltd., Kenogami, Que. White spruce. Middle of tree	5.05	27.42	60.95	1.58	0.94	23	Sound

[1] Calculations were made on oven-dry weight of samples of wood.

lignin or noncellulose in sound spruce wood, these constants were determined on a large number of samples obtained from various parts of the United States and Canada.

These samples of sound wood were first examined microscopically by an independent investigator in order to determine their soundness. Slides were made of samples taken from the center of the tree to the circumference. The annual rings were also carefully counted. In Table I are given the results of several determinations made on the samples of wood, together with the locality from which they came.

It was found that the cellulose and lignin content of sound spruce woods varied considerably, depending upon the location in which they were grown. The cellulose content of the samples of spruce woods grown in the northeastern part of the United States and in Canada was much higher than in those grown in Minnesota and Wisconsin. The sample of spruce wood from Mellon, Wis., analyzed by A. W. Schorger[7] showed a very high cellulose content (61.85 per cent); however, this sample was not prepared for analysis in the manner described in this paper. It may also be noted that the spruce wood secured from Edmunton, Alberta, Canada, by the Port Huron Sulphite and Paper Company of Port Huron, Mich., gave the highest cellulose content, although it contained an occasional thread of mycelium or decay. However, since the pulping trials and other chemical studies were made on infected woods from Wisconsin, it seemed advisable not to take the averages of the analytical constants obtained from all of the sound spruce woods, but to use a sound Wisconsin spruce wood as a standard for comparison. The sample of fresh "sound white spruce," from the Marathon Paper Mills Co., Rothschild, Wis., was chosen as a standard for sound spruce, with which other results from the analyses of decayed wood are to be compared, because it was found not to contain any infection or decayed materials. The data on check analyses are given in Table II.

TABLE II—RESULTS OF ANALYSIS OF SOUND WHITE SPRUCE WOOD FROM ROTHSCHILD, WISCONSIN

Sample No.	Cold-Water-Soluble	Hot-Water-Soluble	Ether-Soluble	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl-pentosan	Ash	Moisture
V-A	2.25	3.83	...	8.80	18.91	...	...	58.50	63.55	10.37	26.08	11.88	1.88	0.17	3.17
V-A	2.30	3.90	1.24	8.83	18.90	4.14	28.30	58.40	...	...	...	...	...	...	...
Av.	2.28	3.87	1.24	8 82	18.90	4.14	28.30	58.50	63.55	10.37	26.08	11.88	1.88	0.17	3.17

TABLE III—RESULTS OF ANALYSIS OF SOUND AND INFECTED SPRUCE WOODS

Kind of Wood (Spruce)	Cold-Water-Soluble	Hot-Water-Soluble	Ether-Soluble	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl-pentosan	Ash
Sound spruce V-A, Rothschild, Wis.	2.25	3.83	...	8.80	18.91	4.14	...	58.58	63.55	10.37	26.08	11.88	1.88	0.17
Average	2 30	3.90	1.24	8.83	18.80	...	28.30	58.40	...	...	...	...	...	...
White spruce No. 2549, Cloquet, Minn. Very slightly infected	3 47	5.61	1.58	15.07	24.00	5.55	30.60	54.60	...	...	...	...	...	0.38
Slightly infected No. 2545 Marathon, top of pile, mill run	4.19	6.39	1.71	20.64	28.54	7.74	30.51	54.18	42.86	37.68	19.46	11.31	1.63	1.37
Infected No. 2546 Marathon, bottom of pile	5.54	9.75	1.38	39.92	49.28	17.48	35.21	46.90	27.75	61.45	10.80	9.45	2.66	0.75
Badly infected spruce No. 2541 Brokaw	6.58	11.92	1.47	44.00	62.36	23.57	38.20	42.00	17.00	74.60	8.40	8.50	3.77	0.61
Dead head spruce No. 2556, Sartell, Minn.	1.41	1.34	0.59	12.00	19.70	5.97	30.96	59.5	60.00	16.10	23.90	9.81	2.84	0.45

DISCUSSION OF THE ANALYSES OF SOUND AND DECAYED SPRUCE WOODS

In Table III are listed the more important chemical constants of the five typical spruce woods described above. There are also included in this table the data on the analysis of a "dead head" or water-logged sample of spruce wood.

The cellulose content of the wood decreases very considerably with increased decay. Taking the extremes of the sound and infected wood, we find such results as 59.50 and 42.00 per cent, respectively, in the total cellulose content for Wisconsin woods. Although the difference in the cellulose content is comparatively large in the decayed woods as compared with the sound, far more indicative of the amount of decay is the fact that the cellulose obtained from the decayed woods is not as stable or as resistant toward chemical reagents as that obtained from sound woods. Practically 60 per cent of the cellulose from sound wood is stable, or the so-called α-cellulose, whereas, only 17 per cent of the small cellulose content of decayed wood is α-cellulose. This ratio of one-fifth as much stable cellulose in the decayed wood as in the sound, and the low chemical resistance of the unstable celluloses found in the decayed woods, would tend to explain the small yields obtained from pulping decayed woods, especially in the soda and sulfate processes. As the process of decay progresses, there is a very marked increase in the less stable or β-cellulose. This appears to be due either to the metabolism of the organisms of decay or to the action of enzymes, produced by these organisms, on the cellulose. The increase in β-cellulose in extremely decayed over sound woods is approximately 60 per cent of the cellulose. This very large

TABLE IV—RESULTS OF ANALYSIS OF THE CORRESPONDING "SULFITE PULPS" FROM SPRUCE LISTED IN TABLE II

KIND OF WOOD	Cold-Water-Soluble	Hot-Water-Soluble	Ether	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl-pentosan	Ash
No. 2561 paper from sound white spruce, typical	0.15	0.00	1.12	11.02	20.53	3.05	1.26	97.25	87.50	3.19	9.31	3.55	0.89	0.29
No. 2547 paper from No. 2545 Marathon (top of pile) wood	0.00	0.00	1.59	10.85	24.89	2.66	2.80	96.17	75.83	17.85	6.32	4.61	0.60	0.57
No. 2548 paper from No. 2546 Marathon (bottom of pile) wood	0.00	0.00	1.01	13.46	31.39	3.78	2.19	96.18	72.96	22.00	5.04	3.69	1.47	0.50
No. 2555 paper from No. 2541 Brokaw infected wood	0.32	5 00	0.91	31.90	52.80	9.05	1.73	94.44	46.05	48.62	5.33	2.97	1.43	0.81
No. 2560 Nekoosa-Edwards wood comparable with No. 2547 or Marathon (top of pile)	0.37	0.00	1.36	14.32	28.20	3.87	1.58	96.50	79.40	11.40	9.20	4.25	0.94	0.33

TABLE V—RESULTS OF ANALYSES OF "SODA PULPS" FROM SOME OF THE SPRUCE WOODS

KIND OF PULP	Cold-Water-Soluble	Hot-Water-Soluble	Ether	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methyl-pentosan	Ash
No. 2559 paper from infected Nekoosa-Edwards spruce	0.86	0.19	1.02	3.23	6.59	2.58	9.64	89.42	57.10	39.10	3.80	7.80	0.70	1.17
No. 2557 paper infected Brokaw wood No. 2541	0.65	0.00	0.72	7.01	13.64	7.92	38.32	56.43	23.36	69.66	6.98	4.58	2.77	2.08

difference in extreme cases of decay points out very clearly how the progress of decay of spruce may be observed by this determination.

RESULTS OF THE CHEMICAL ANALYSIS OF PULPS MADE FROM SOUND AND DECAYED SPRUCE BY THE SULFITE PROCESS

These spruce woods, together with a sample of infected wood from Port Edwards, Wis., were separately subjected to pulping by the sulfite process, in the small digester at the Forest Products Laboratory. The pulp was run into waterleaf paper on the small experimental paper machine and the samples thus obtained were chemically analyzed, by the same methods of procedure as in the case of the woods.

It will be noted in Table IV that the cellulose content of pulp made from these woods by the sulfite process decreased with increased decay. But the difference is not so marked as in the woods themselves. There is a difference of only about 3 per cent in the most extreme cases. The α-cellulose, however, indicates again how far the decay had advanced in the woods previous to pulping. There is only one-half as much α-cellulose in pulp made from the badly rotted wood as in the pulp made from sound wood, or, in other words, the decrease is from 87.50 per cent to 46.05 per cent.

There is a great difference in the β-cellulose content of waterleaf pulp made from sound and decayed woods. In pulps made from sound wood, the β-cellulose is only 3 per cent of the total cellulose, while it is 48.62 per cent of the total cellulose in paper made from decayed wood. The proportion of γ-cellulose in the total cellulose content remains practically constant in pulps made from sound and decayed woods. This would tend to show that the γ-cellulose had been practically removed by the drastic treatment of the woods during the pulping process. The amount of γ-cellulose obtained in the determinations is probably due to the action of the alkali on the original "Cross and Bevan" cellulose. The fact that a second treatment of the α-cellulose with 17.5 per cent sodium hydroxide gives an additional loss of 5 per cent (as proved by the authors and also shown by C. G. Schwalbe and Becker[9]) would tend to show that a small amount of γ-cellulose is possibly formed by the action of the alkali, even though it is completely removed during the pulping process. The additional fact that γ-cellulose is easily hydrolyzed also points to the fact that γ-cellulose was practically removed by the pulping process.

CELLULOSE DETERMINATIONS—In studying the pulping characteristics of sound and decayed woods by the soda process (data of which will be given in a later publication), it was found that the pulp made from badly rotted wood (Sample 2541, Table III) was very raw (brash and dirty). This was because the wood neutralized or made inactive practically all of the alkali before the cook had reached completion. It may be pointed out here that there is a tremendous loss in chemicals when decayed wood is pulped by the soda process. This point will be taken up in greater detail in the discussion of the results of the action of dilute and strong alkali solutions on sound and decayed woods and pulps.

It will be noted in Table V that the pulp made from badly rotted wood by the soda process has a very low cellulose content (56.43 per cent) as compared with pulp from only partly decayed wood (89.42 per cent).

RESULTS OF CHEMICAL ANALYSIS OF PULPS MADE FROM SOUND AND DECAYED SPRUCE BY GROUNDWOOD PROCESS

Two samples of spruce wood, one representing a practically sound Wisconsin spruce ground daily at one of the large Wisconsin mills, and the other representing badly rotted wood taken from the bottom of a pile of logs, were subjected to pulping by the groundwood process at one of the coöperating mills.

These samples, together with a sample of sound pulp, were inoculated with a wood-destroying fungus and stored for 6 mo. in a constant temperature and humidity room before analysis. The data in Table VI show that the cellulose content of sound groundwood pulp is practically the same as that of pulp made from badly rotted wood, *e. g.*, 60 and 59.69 per cent, respectively. These results may appear surprising at first. However, if the small yield (78.5 per cent) obtained and also the value of the pulps resulting from the use of badly rotted woods, as compared to that of sound wood, is taken into consideration, one can easily see the tremendous losses which must be sustained by the mills from the use of decayed woods.

The cellulose content remains practically constant because of the large percentage of cold- and hot-water-soluble products found in the rotted woods. These values make up the large amounts of material found in the "white water" which is a direct loss to the manufacturer.

Sample 26 of groundwood pulp (Table VI) made from sound spruce wood infected with a wood-destroying fungus gave a very decided decrease in the cellulose value, *e. g.*, from 60.00 per cent to 43.00 per cent. S. A. Mahood and D. E. Cable[10] have indicated that the cellulose content of infected groundwood pulp is reduced. The cellulose content of the two pulps made from sound and infected woods, when stored in the fungus pit for 6 mo., showed a greater decrease in the case of the pulps made from wood that was already infected than that made from sound wood. This fact, together with the evidence shown in Table VI, brings out more plainly the losses involved in using infected wood, especially in cases where the pulp is to be stored for any length of time.

The α-, β-, and γ-celluloses in these pulps, made from sound and infected woods, remain practically constant, while pulp that has been infected and stored for 6 mo. after manufacture shows a large decrease in α- and γ-cellulose and a very decided increase in β-cellulose.

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[9] *Paper*, **27** (1921), No. 25, 21.

[10] "A Chemical Investigation of Sound and Infected Groundwood Pulp," *Paper*, **25** (1920), No. 24, 11.

Table VI—Results of Analyses of the Corresponding "Groundwood Pulps" from Woods in Table III

Kind of Pulp	Cold-Water-Soluble	Hot-Water-Soluble	Ether	1 Per cent NaOH	7.14 Per cent NaOH	Copper No.	Lignin	Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose	Pentosan	Methy-pentosan
No. 2544 sound groundwood corresponding to No. 2545 Marathon wood (top of pile)	0.00	1.00	0.41	10.13	18.28	4.44	31.00	60.00	60.53	24.48	14.99	11.96	2.01
No. 2558 paper groundwood Marathon (bottom of pile) No. 2546	0.68	1.45	0.786	17.72	27.43	6.63	29.74	59.69	58.69	26.71	20.60	10.37	2.65
No. 26 groundwood pulp infected with wood destroyers and stored for 6 mo. in sterile bottles	6.94	11.06	0.16	47.40	62.80	23.90	35.30	43.00	31.35	63.20	5.45	8.44	3.04

General Discussion of Constants Obtained by Complete Chemical Analysis of Sound and Decayed Spruce Woods and Pulps Made Therefrom by the Three Processes

CELLULOSE—The data obtained from the complete analysis of sound and infected woods and pulps indicate quite clearly that the wood and pulp in most cases of extreme decay breaks down, as might be expected, by a more or less selective action of the organisms.[11] That the organisms, especially the wood destroyers, attack the cellulose to a larger extent than the noncellulosic material is shown by the large decrease in cellulose and the apparent increase in the noncellulosic material or lignin. The words "apparent increase" are used because the lignin content remains nearly constant during decay, if the loss in weight of the decayed wood is taken into consideration and the results of the lignin determinations are based on the weight of the original sound wood. In other words, the actual weight of lignin obtained from a definite weight of sound wood remains practically the same after the wood has decayed. This selective action on the cellulose is especially marked in the case of badly decayed groundwood pulps inoculated with wood destroyers. The data indicate plainly that as the decay progresses the percentage of cellulose decreases, but far more indicative of the progress of decay is the decrease in the amount of the α- or stable cellulose, and the very decided increase in the percentages of the β- or less stable cellulose. The decrease in the amount of γ-cellulose would show that the cellulose is broken down by the process of decay into the less stable or less resistant β- and γ-celluloses. But since γ-cellulose occurs in smaller amounts in decayed woods than in sound wood and pulp, it would appear that the γ-cellulose is a transition form of cellulose and is broken down into simpler compounds much more rapidly than it is formed by the action of the organisms of decay. It would appear, from the foregoing statements, that fungus cellulose is composed mainly of the two less stable celluloses, *e. g.*, β- and γ-, since these two celluloses and their cleavage products are most abundant in decayed woods and pulps.

LIGNIN—The results in Table I show that the lignin content or the noncellulosic material of spruce wood, as determined by a modification of the Ostand Wilkening[12] method, bears a more or less direct relation to the cellulose content in sound spruce woods. In other words, the ratio of lignin to cellulose is practically constant. This relation appears to be independent of the locality where the woods were grown, or the rate of growth or the age of the tree. However, in infected woods (Table III) this relation does not hold in all cases, as was shown in the discussion under cellulose. The extreme case of sound and badly rotted wood shows an increase of 10 per cent in lignin.

The lignin content of the sulfite pulps made from sound and infected woods remains nearly constant and depends upon the cooking conditions applied in reducing the wood to pulp. This may also be said of the lignin remaining in the pulps made by the soda and sulfate processes. The high lignin content of 38.32 per cent in soda pulp from the badly rotted wood is a result of the raw cook, due to the fact that the wood neutralized the alkali, practically at the beginning of the operation. The slight increase in lignin content in infected groundwood pulp is due to the larger hot- and cold-water-soluble materials in the decayed wood.

HOT- AND COLD-WATER-SOLUBLE CONSTANTS—These constants increase to a very great extent with the increase in decay of wood and pulp. Mahood and Cable[11] found that the water-soluble content of groundwood pulp increased as a result of infection. Taking for example the extremes of the sound and infected wood, there are such differences as 3.83 and 11.92 per cent hot-water-soluble material and 2.25 and 6.58 per cent cold-water-soluble material. If one takes into consideration the tremendous loss of practically 12.00 per cent of the total wood, when pulping infected woods, one can see what this means to the manufacturer. The greatest losses occur in the groundwood process. A mill run on sound and infected spruce showed yield figures on a weight basis of 84.5 and 78.5 per cent, respectively, and on a cord basis a yield of 390 lbs. more per cord of sound wood than were obtained per cord of infected wood. Aside from these actual losses there is a very decided further loss from the decrease in quality of the stock made from infected wood, which, however, cannot be accurately estimated. In Table VI (Sample 26) it is shown that another 11 per cent hot-water-soluble loss is sustained when infected pulp, stored for 6 mo., is reduced to paper.

ETHER-SOLUBLE MATERIAL—According to the data on both spruce woods and pulps, the ether-soluble material, consisting of resins, waxes, etc., does not change materially with increased decay; hence, this determination is not a criterion of the progress of decay.

ALKALI-SOLUBLE MATERIAL—The values obtained upon treating the woods and pulps with solutions of 1 per cent and 7.15 per cent sodium hydroxide show, in general, that the infected woods are less resistant to alkaline reagents. There are very decided increases in solubility with the progress of decay, when sound and infected woods and pulps made from them by the sulfite, soda, and groundwood processes are treated with the two concentrations of alkali. Such differences as 18.91 and 62.36 per cent strong-alkali-soluble were found in sound and infected wood, respectively. The increase in alkali solubility with increase of decay was almost as striking in the case of sulfite pulps made from these woods.

In reducing the badly rotted wood to soda pulp, under the same cooking conditions as were used for sound wood, the alkali liquor was neutralized or made inactive practically at the beginning of the cook. This resulted in a very raw cook. These results are confirmed by E. Sutermeister in a recent publication.[13] The resulting pulp, as would be expected, gave a very high alkali solubility compared with that obtained from pulp made from slightly infected wood.

The alkali solubility values, obtained on groundwood pulp made from these woods, showed an increase with increased decay. These values, however, are not as high as those resulting from direct treatment of the woods. This wide variation is accounted for in the fact that in the one case the analysis was made on waterleaf paper made from the pulp and in the other on the wood. In the drastic treat-

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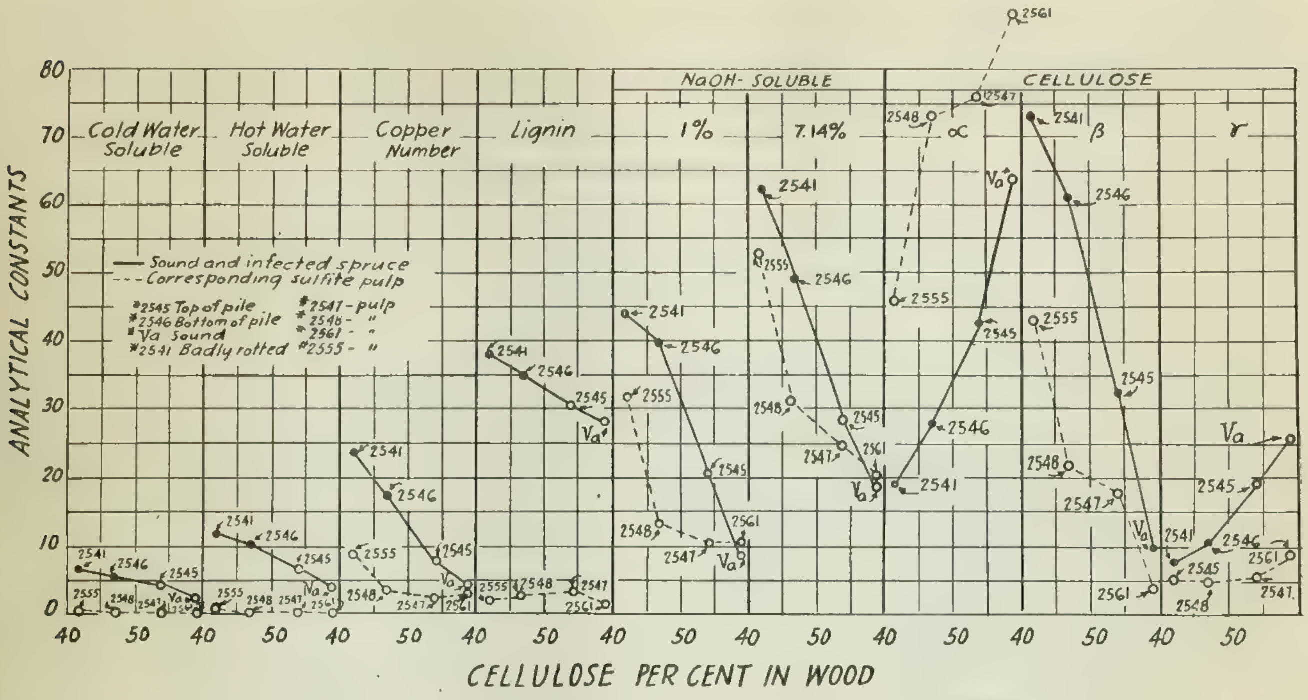
[11] This is also shown in the work of B. Johnsen and R. W. Hovey, *Paper*, **21** (1918), No. 23, 46.

[12] *Chem.-Ztg.*, **34** (1910), 461; Cross and Bevan, "Researches on Cellulose," **III** (1905–10), 39.

[13] "Decay of Pulpwood and Its Effects in the Soda Process," *Pulp Paper Mag. Can.*, **19** (1921), 733.



Analytical Constants for Sound and Infected Spruce and Corresponding Sulfite Pulp

ment of beating and screening and repeated washings, the finer particles which show the greatest solubility in alkali are removed.

The extremely high value of 62.80 per cent strong-alkali-soluble, obtained from groundwood pulp (Sample 26, Table VI) infected with a wood-destroying fungus and stored for 6 mo. in sterile bottles at constant temperature and humidity, again shows a direct comparison between sound and infected woods and pulps.

COPPER NUMBER—This value is a measure of the reducing power of the woods and pulps. The data show a large increase in this value with increased decay in the woods. The difference in this value for pulps is not nearly as marked except in the case of infected groundwood pulp, where the copper number is as large as is obtained from badly rotted spruce wood. The large copper values in the decayed woods and pulps are due to the cleavage products formed by the action of the organisms of decay, and possibly to some extent to the increase in lignin.[14]

PENTOSANS AND METHYLPENTOSANS—The yields of pentosans obtained from the sound and infected spruce woods appear to decrease with the progress of decay, while the methylpentosan content increases with decay. The percentages obtained from pulps made from sound and decayed spruce wood give no uniform values from which conclusions might be drawn.

Although the values of these chemical constants are a measure of the content of pentosans which are obtained by the Tollens method,[15] a number of compounds introduce an error in this determination. Oxycellulose, oils or waxes, and fatty decomposition products[16] yield furfural, the error of which is difficult to eliminate. Although a correction to lessen this error has been worked out, it may be seen that the difficulty encountered lies in obtaining an accurate knowledge of amounts of each one of the compounds which introduce the error.

ASH—The results of this determination are of little value, because the mineral content of woods remains practically unchanged during decay.

Relation of Analytical Constants to Per cent Cellulose

The results given in the figure show at a glance the large losses in woods and pulps due to infection and decay, and indicate how the chemical constants increase or decrease with the progress of decay.

The cellulose content of woods and pulps is undoubtedly the constant of most vital importance in the manufacture of paper. This value has, therefore, been used as a basis for plotting the other analytical constants.

Conclusions

The conclusions from the chemical standpoint which may be drawn from this work are that in all cases the infected woods produce less pulp per unit weight of wood than the sound woods.

The inferiority of the infected woods over the sound woods are:

1—The cold- and hot-water-soluble materials increase during decay and are a direct loss to the mills.

2—Higher alkali-soluble materials are found, showing a lower resistance to the action of chemical reagents. This would be very noticeable in a soda or sulfate mill, because more alkali than would be necessary for sound wood would be required to accomplish the same result.

3—There is an increase in copper number showing that infected wood contains a greater amount of reducing compounds.

4—In most cases of extreme decay, the rate of dégradation of lignin and cellulose is selective and not uniform.

5—Lower percentage of α- or stable cellulose, higher percentage of β- or less stable cellulose.

The large losses sustained in converting infected woods into pulps, together with the additional losses of further converting these pulps (made from infected woods which undergo further decomposition when stored) into paper, have been pointed out.

The paper made from decayed woods and pulps is dirty, brash, and has very little strength. It requires more sizing, offers difficulty in sticking to the couch and press rolls, and foams excessively.

The yield of finished paper is greatly reduced, while the cost of production is increased, because the decayed chips occupy the same space in the digester and use, therefore, the same amount of chemical as the sound wood, and in some cases more. Decayed wood also requires the same expenditure in grinding.

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[14] E. Heuser, "Determination of Lignin," *Paper*, **27** (1921), No. 23, p. 24.

[15] Ellett and Tollens, *J. Landw.*, **53** (1905), 20.

[16] Browne, "Handbook of Sugar Analysis," 452.

When it is remembered that the pulp yield on Northern woods is directly proportional to the weight per cubic foot, it becomes clear that the purchase of wood weighing 28 or 24 lbs. per cubic foot makes a decided difference in the weight of actual wood cooked per day.

The Determination of the "Bromine Figure" or "Chlorine Factor" of Pulp, and the Utilization of These Quantities in Bleaching[1,2]

By **Alfred Tingle**

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The object of the work here described was to find a method whereby the bleaching quality of sulfite spruce pulp could be determined. The point immediately considered was how much available chlorine should be consumed per unit weight of a given shipment of pulp, and the time factor, which is also likely to vary with different pulps, was not inquired into. It was desired, first, to be able to direct the workman as to the amount of bleach he should use and to have a check upon him should he indulge in extravagant practices, and, secondly, to be able to apportion blame between the maker of the pulp and the bleacher, should the consumption of chlorine rise above an economical figure.

This first object has only partly been attained at present. Owing to the fact that the pulp must be dried before any result can be obtained, the process consumes much time when applied to routine control work. It can, also, be used only by a man versed in careful analytical procedure.

The second object has been fully attained, to judge by the results in this laboratory and mill. Its general utility and final reliability can, however, not be settled by work done in a single laboratory, where of necessity the pulps examined are of only a few types. The work is now published in the hope that it may be duplicated elsewhere, receiving criticism and, if necessary, condemnation as the result of extended experience.

Preliminary Considerations

CHOICE OF REAGENTS—There seemed to be three possible classes of reagent by which the chlorine-consuming power of a pulp might be measured, *viz.*, (1) compounds which react specifically with lignone, and supposed to give condensation products, (2) oxidizing agents, and (3) halogens or halogen-producing compounds.

Cross and Bevan's phloroglucinol reaction might be considered as a type of the first class. It was dismissed as too tedious and probably not sufficiently sensitive. Preliminary experiments showed that nothing could be based on the absorption of an aniline salt from its solution by lignone. The quantity of amine thus withdrawn is small in proportion to the lignone present, and the action is possibly one of solid solution rather than chemical combination.

In Class 2, potassium ferricyanide was tried, while mixtures of potassium permanganate or dichromate with hydrochloric acid may be considered as belonging to either Class 2 or 3, according to the concentration of the solutions used. In all three cases it was found that under experimental conditions leading to the attack of lignone, cellulose was also attacked, generally to a marked degree; if action was so moderated as to leave cellulose unacted upon, the lignone remained also little attacked.

More definitely in Class 3 come chlorine and the hypochlorites, bromine and its related compounds, and iodine chloride. The latter was experimented with dissolved in (*a*) acetic acid, (*b*) hydrochloric acid, and (*c*) carbon tetrachloride, and (*d*) in the form of Hubl's solution applied under a variety of conditions. In general it may be said that when concordant results were obtained they showed either that no action had taken place, or that the action was equivalent to the use of ordinary iodine solution.

The use of chlorine or a hypochlorite involves certain manipulative difficulties and is made the more undesirable from the constant change in titer of such solutions. They have been worked with extensively, but no accurate and accepted method involving their use has yet been evolved.

Bromine does not present quite so many difficulties at first sight. While the titer of bromine water does not remain constant, a solution of bromine in alkali will, over considerable periods, give the same amount of bromine when acidified. Thus what is equivalent to a permanent standard solution of bromine can easily be prepared, though it can be used only in acid media. The relative extent of action of bromine on lignone and cellulose is not well known, and experiments made to elucidate this point were not at first concordant.

THE MEANS OF OVERCOMING DISCREPANCIES—As experiments were continued it became apparent that discordant results had a purely mechanical origin. Liquid reagents were acting upon a solid pulp; a solid, too, which had in some cases been rendered very nonabsorbent in the drying process to which it had been subjected. In some cases reaction did not proceed throughout the mass, while in others the reacting liquid held in the pores of the solid differed in composition from the main volume. Experiments were then made, in the course of which the cellulose was completely dissolved before addition of the reagent, and concordant results became the rule.

The solvent chosen was a mixture of 9 volumes HCl (sp. gr. 1.19) to which was added 1 volume H_2SO_4 (sp. gr. 1.84). The mixture could be made before being added to the pulp, but in some cases solution was better effected by first saturating and disintegrating the pulp with hydrochloric acid, then adding the requisite amount of sulfuric acid, which formed a gelatinous but clear solution. When water was added, cellulose was precipitated from this solution in such a fine state of division that it was readily penetrated by reagents.

Any chemical change in the cellulose which may accompany these physical changes is not important in the present work so long as the new products are, like the cellulose, unattacked by the reagents used in determining the lignone.

Experiments made with hypochlorites, even after the adoption of this solvent, continued to give discrepant results. This was attributed, at least in part, to the mechanical loss of chlorine, which could be avoided only by using elaborate apparatus. Bromine was not subject to this difficulty and experiments were continued with that reagent.

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[1] Presented before the Section of Cellulose Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Received May 28, 1921.

Interaction of Bromine and Dissolved Pulp[3]

ACTION OF BROMINE ON DISSOLVED CELLULOSE—Filter paper of various standard grades was taken as sufficiently pure cellulose for the purpose. Weighed quantities of the paper were dissolved in acid and a measured volume of bromine solution was added to each. After standing in tightly stoppered vessels for a predetermined time, excess of potassium iodide was added. The mixtures were then largely diluted, and the free iodine titrated. The details of manipulation were the same as those described below for the investigation of unbleached pulps.

It had been assumed that all these filter papers would be of thoroughly bleached stock and free from antichlor. The results, as shown in Table I which follows, did not quite bear out that belief. Expts. 1 to 5 on Sample A show that some constituent was present which reacted with bromine, but that this reaction was completed within the first 90 min. and was almost completed within the first 40 min. Had the action been between bromine and cellulose, it would not have so quickly come to an end. Sample B (Expts. 6 and 7) reacted with bromine to a less extent, the reaction being completed in 30 min. or less. The remaining three samples of paper seem to be purer cellulose and showed no reaction with bromine in 30 min. or more. It seems a safe conclusion that, under the experimental conditions, bromine does not react with cellulose itself.

Table I

Expt. No.	Weight of Filter Paper Gram	Time of Action of Bromine Min.	0.1 *N* Bromine Solution Consumed Cc.	Sample of Filter Paper Used
1	0.6025	40	0.6	A
2	0.6635	60	0.7	
3	0.6685	90	0.8	
4	0.6635	120	0.8	
5	0.6953	150	0.8	
6	0.5878	30	0.3	B
7	0.5840	90	0.3	
8	0.5210	30	0.0	C
9	0.5458	40	0.0	
10	0.5300	60	0.0	
11	0.5730	120	0.1	
12	0.6356	30	0.0	D
13	0.6413	30	0.0	E

ACTION OF BROMINE ON UNBLEACHED SULFITE SPRUCE PULP—Experiments were made in a manner similar to the foregoing, substituting an unbleached sulfite spruce pulp for the "pure" cellulose. Samples were in every case taken from the same small sheet of pulp, the only variation in the experiments being the time factor. The results were calculated to a common basis for which the term "bromine figure" is suggested. This is defined as the weight in grams of pulp which reacts with 1 cc. of 0.1 *N* bromine solution. The "bromine figure" calculated from each determination is shown in the fourth column of Table II. It should be remarked that where several determinations have been made for a given time of action, they have been made on different occasions and under as widely different circumstances as the method of manipulation can permit.

A study of these figures led to the following conclusions:

1—More than 50 per cent of the reaction takes place in the first 10 min.

2—After 20 to 30 min. there is a pause in the changes which occur. It seems as though a definite stage in the reaction were reached, and as though no further bromine was consumed till this stage was completed.

3—*For this 30-min. time interval all determinations on the same pulp agree very closely.*

4—After the stage which is reached in 30 min. the reaction becomes more irregular. Determinations made at the end of a 60-min. period show poor agreement *inter se.*

Table II

Expt. No.	Weight of Dry Pulp Gram	0.1 *N* Bromine Solution Consumed Cc.	"Bromine Figure"	Total Time of Action of Bromine Min.
1	0.6086	5.15	0.118	10
2	0.5745	5.15	0.111	20
3	0.6460	5.75	0.112	30
4	0.6413	5.75	0.111	
5	0.6278	5.65	0.111	
6	0.6390	6.00	0.106	40
7	0.6245	5.85	0.106	60
8	0.6345	6.60	0.096	
9	0.7257	6.60	0.110	
10	0.6970	7.20	0.096	90
11	0.6925	7.00	0.099	
12	0.7170	7.20	0.099	
13	0.7520	7.80	0.096	120
14	0.6865	7.10	0.096	150

5—After 90 min. the reaction appears to be complete. Bromine figures calculated for 90, 120, and 150 min. show a fair agreement.

THE "THIRTY-MINUTE BROMINE FIGURE" AND THE "CHLORINE FACTOR" CONSIDERED AS CONSTANTS—Examination of other pulps confirms the deduction that the bromine which reacts in 30 min. is a fairly definite constant. Analytical results can be calculated into another form, however, which is more convenient for ultimate use than the bromine figure. The quantity, which has been named the "Chlorine Factor" of a pulp, is defined as the weight of chlorine equivalent to the bromine reacting with 100 parts of pulp in 30 min. This is obviously $\frac{100 \times 0.0035}{\text{bromine figure}}$, or more directly

$$\frac{100 \times 0.0035 \times \text{cc. of } 0.1\ N \text{ Br consumed}}{\text{weight of pulp sample}}.$$

The results of determinations of these constants on six pulps having very different histories are given in Table III and show the extent of agreement which may be expected.

Table III

Expt. No.	Weight of Dry Pulp Gram	0.1 *N* Bromine Solution Consumed Cc.	"30-Minute Bromine Figure"	"Chlorine Factor"	Sample No.
1	0.6135	3.60	0.1704	2.083	A
2	0.7160	4.20	0.1704	2.082	
3	0.6570	3.30	0.1990	1.783	B
4	0.6490	3.30	0.1966	1.805	
5	0.5267	4.70	0.1120	3.168	C
6	0.6880	5.90	0.1166	3.044	
7	0.7575	6.80	0.1114	3.186	D
8	0.7795	7.10	0.1098	3.233	
9	0.7722	4.40	0.1755	2.023	E
10	0.7347	4.20	0.1749	2.029	
11	0.6278	5.65	0.1111	3.194	F
12	0.6413	5.75	0.1112	3.183	
13	0 6460	5.75	0.1123	3.159	

The determinations on Sample C do not agree as closely as they should, but in setting forth this work no eliminations have been made except where a known fault of manipulation has led to obvious error.

The difference between the determinations on Sample D amounts to 0.047 in the chlorine factor. When the practical application of the constant is explained, it will be seen that this difference has slight significance.

Utilization of the "Chlorine Factor"

It is obvious enough that the chlorine factor is not the weight of chlorine required to bleach 100 parts of pulp. The experience of this mill is that it does bear a simple and definite relation to the latter quantity.

It is now suggested that for a well-washed pulp the weight of chlorine required to bleach 100 lbs. dry weight = chlorine factor × K.

It may be found that K varies according to the practice of different mills. As bleaching is carried out at the mill where these experiments were made, the value determined is 3.

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[3] In the following experiments it must be understood that by "decinormal bromine solution" is meant a solution of bromine in dilute alkali, of such strength that when added to an acid medium it liberates the amount of bromine contained in the same volume of decinormal bromine solution.

Thus, a certain pulp was found to have consumed 6.03 lbs. of chlorine per 100 lbs. of dry material, in the ordinary run of mill practice, excess of bleach being added and the amount of this excess determined. The same washed pulp showed a chlorine factor 2.026, so that the calculated weight of chlorine required to bleach 100 lbs. was 6.078 lbs. Agreement of theory and mill practice could not well be closer.

It need hardly be said that bad methods such as negligent washing, excessive temperature, etc., will affect the apparent value of K. Whether its value will be the same in every well-conducted mill can be decided only by the extended observations of many competent observers. It would be of great interest to know also whether this method is applicable to pulps of entirely different types made from different woods and by different processes. It is too early to speculate as to whether the fact that $K=3$ (at least for certain bleaching methods) has any theoretical significance, but if this value is found to be a general one, a theoretical reason might be suggested.

Detailed Description of Analytical Method

PREPARATION OF BROMINE SOLUTION—Add 8 g. of bromine to 100 cc. N NaOH solution, agitate till solution is complete, then boil. When cool, dilute to 1 liter. Standardize by adding potassium iodide to a known volume, acidifying with hydrochloric acid and titrating the liberated iodine against 0.1 N sodium thiosulfate solution.

The above product remains for weeks without appreciable change in strength and when run into an acid solution is equivalent to a 0.1 N solution of bromine.

PREPARATION OF "ACID SOLVENT"—Into a flask containing 450 cc. of hydrochloric acid (sp. gr. 1.19) pour slowly 50 cc. of sulfuric acid (sp. gr. 1.84). Mix thoroughly and allow to cool. This mixture will generally gelatinize and dissolve pulp in a few minutes. Sometimes, especially when the pulp has not been evenly compressed, it is better dissolved by adding the acids separately and successively in the reaction vessel, allowing the hydrochloric acid to disintegrate the pulp before the sulfuric acid is added.

ANALYTICAL PROCEDURE—Weigh the dry pulp (0.6 to 0.75 g.) into a dry flask or bottle (about 200 cc.) having a well-ground glass stopper. Add 30 cc. of the "acid solvent" described above and agitate till solution is complete, or add 27 cc. of hydrochloric acid (sp. gr. 1.19), shake till the pulp is disintegrated, add 3 cc. of sulfuric acid (sp. gr. 1.84), and shake again. It is essential at this stage that the solution be quite free from hard, unchanged cores of pulp. When uniformity has been obtained, add a measured volume (20 or 25 cc.) of the alkaline 0.1 N bromine solution, shake well, and allow to stand for 30 min. with occasional gentle agitation. Check the reaction by adding 2 g. of potassium iodide dissolved in about 25 cc. of water and shaking well. Dilute as largely as the capacity of the reaction vessel renders convenient, and titrate with 0.1 N sodium thiosulfate. Toward the end of the titration starch paste may be added advantageously, but disappearance of the blue color is *not* a sign that the end-point has been reached. There remains a little iodine dissolved in the finely divided cellulose, to which it gives a reddish brown tint. The thiosulfate should be added very slowly toward the end, and each addition should be followed by prolonged and very vigorous shaking. Finally the red tint of the cellulose precipitate disappears, leaving a cream-colored or white suspension. This, the true end-point, can be read within 0.1 cc. after a little practice, and back-titration with 0.1 N iodine solution can be resorted to in case it is overrun. Persistence of blue or purple spots after all other color has disappeared is due to the pulp not having been thoroughly disintegrated by the acid solvent. The titration will be untrustworthy in proportion as these spots are large and numerous; the iodine which they contain leaches out only slowly and somewhat imperfectly—too slowly to make a good titration possible.

CALCULATION OF RESULTS—This is best shown by an actual example.

Weight of dry pulp = 0.7722 g.
Volume of alkaline bromine solution = 20.0 cc.
Standardization showed 20 cc. bromine solution = 21.1 cc. 0.1 N $Na_2S_2O_3$
Buret reading after titration of pulp = 16.8 cc. 0.1 N $Na_2S_2O_3$
Bromine consumed by pulp = 4.3 cc. 0.1 N solution

$$\text{"Bromine figure"} = \frac{0.7722}{4.3} = 0.1796$$

$$\text{and "Chlorine factor"} = \frac{4.3 \times 0.00355 \times 100}{0.7722} = 1.977$$

Summary

1—The extent to which bromine solutions, approximately decinormal, act on cellulose and on unbleached sulfite spruce pulp has been investigated.

2—It is found that accurate measurements are possible only when the material is brought into solution, *e. g.*, by certain mineral acids, before treatment with bromine.

3—Under these circumstances there is no reaction between bromine and cellulose within 30 min.

4—Reaction between bromine and pulp (containing lignone) seems to proceed in definite steps, one of which is completed within 30 min.

5—From measurements of this action, a quantity is found which bears a definite and simple relation to the chlorine consumption in bleaching.

6—The method of manipulation is described in detail.

Civil Service Commission Announcements

The United States Civil Service Commission has announced the following examinations to fill vacancies in the Bureau of Standards: Junior aid at $720 to $840, laboratory apprentice at $540, laboratory assistant junior grade at $1000, senior aid at $900, engineer at $2800 to $4000, associate engineer at $2000 to $2800, assistant engineer at $1500 to $1800, technologist at $2800 to $4000, associate technologist at $2000 to $2800, and assistant technologist at $1500 to $2000. On account of the needs of the Service, applications will be received until further notice. Papers will be rated as received and certification made if the needs of the Service require.

On January 11, March 8, and May 17, 1922, examinations will be given to fill the following vacancies in the Bureau of Standards: Junior engineer at $1200 to $1500, and junior technologist at $1200 to $1500.

On January 11, 1922, the following examinations will be given to fill vacancies in the Chemical Warfare Service, Edgewood Arsenal, Md.: Chemical laboratorian at $1200 to $1500, chemist at $3600 to $5000, associate chemist at $2500 to $3600, and assistant chemist at $1800 to $2500.

For further details in regard to these examinations, application should be made to the U. S. Civil Service Commission, Washington, D. C.

Short Course in Ceramic Engineering

The regular biennial two weeks' short course in Ceramic Engineering will be given next January at the University of Illinois, between the dates of January 23 and February 4. The subjects covered will include elementary physics and chemistry; the origin, classification, winning and refining, and testing of clays; the shaping, drying, and burning of clay products; bodies and glazes; the technology of glass; refractories and refractory products; kiln construction; coal and gas fuels; engines and boilers, dynamos and motors, equipment control; pyrometry; drafting and reading of drawings; and business law.

The complete program will be ready for distribution early in January and copies may be secured by addressing the Department of Ceramic Engineering, University of Illinois, Urbana, Ill. The course is open to all who are interested and can be taken to advantage by any one having a common school education. There are no tuition fees.

Effect of Adding Various Chemicals to Wood Previous to Distillation[1]

By **L. F. Hawley**

FOREST PRODUCTS LABORATORY, MADISON, WISCONSIN

This investigation is a continuation of Palmer's work on "The Effect of Catalyzers on the Yield of Products in the Destructive Distillation of Birch."[2] A new title has been chosen since it is not wished to imply that the action in all cases is truly catalytic and since it is not intended to limit the work to one species of wood.

Aside from Palmer's work, in which the wood was treated with phosphoric acid, the only publication on the subject is a recent short note[3] without details, in which it is stated that when wood is distilled in the presence of three or more parts of lime the acid yield (in form of acetone) is greatly increased. Nothing is said about an effect on the yields of alcohol.

Different distillation methods from those used by Palmer were used in the present study in order to develop a simpler process and one which could be used for maintaining an even mixture of sawdust with insoluble materials such as lime. The sawdust was mixed with the solid material if an insoluble chemical was used or was saturated with a solution of the chemical, then dried if necessary, and pressed into briquets 2 in. in diameter and about 1 in. in thickness. These briquets were distilled in a tube furnace under sufficient mechanical pressure to prevent them from falling apart, and the products were collected and analyzed in the usual manner. This general method of distillation had been used in a previous investigation and was found to be simple and satisfactory.[4]

SILVER MAPLE SAWDUST

PHOSPHORIC ACID—The results of several trials with phosphoric acid are shown in Table I. With wood treated with three different concentrations of the acid (0.5, 1, and 1.5), there was a slight decrease in the yield of alcohol and a slight increase in the yield of acid as compared with untreated wood, although the increase and decrease did not follow a regular order according to the amount of acid used. The increase in yield of acid was not sufficient to make phosphoric acid treatment a promising process, especially since the alcohol was slightly decreased. The only distillation of wood treated with phosphoric acid in which a large yield of acid was obtained reported by Palmer was made by distillation under high pressure, a condition which could not be readily obtained in commercial-sized apparatus. Apparently, the use of phosphoric acid under ordinary conditions of pressure is not promising.

LIME—Lime was tested, mixed with the sawdust both in the form of dry lime and milk of lime. The only noticeable effect of small percentages of lime was a decrease in the amount of acetic acid. With larger proportions of lime, as shown in Table I, there was a noticeable increase in the alcohol yield. This alcohol yield was determined by the specific gravity of a fraction of the distillate after redistillation with alkali and acid. It was, therefore, not a determination of pure methyl alcohol, but included also acetone and other materials with low gravities. Contrary to expectation, this increase in total alcohol, constituents was not due to an increase in the acetone content. Acetone determinations were made in all cases with the results varying only between 0.01 and 0.05 per cent, which is not sufficient to require any further discussion. This corresponds with Bassett's statement that large acetone yields were obtained only when three times as much lime as wood was used.

TABLE I—SAWDUST TREATED AND BRIQUETTED

CATALYST		Alcohol	Acetic	
Chemical	Per cent	Per cent	Per cent	REMARKS
		MAPLE		
......	..	1.61	5.22	Av. of 4 runs
H_3PO_4	0.5	1.51	5.67	Av. of 2 runs
H_3PO_4	1.0	1.24	5.39	
H_3PO_4	1.5	1.55	5.40	
$Ca(OH)_2 \Bumpeq 60\%$ CaO		2.45	0.48	
CaO	60	1.94	0.65	
$CaCO_3 \Bumpeq 40\%$ CaO		2.08	4.69	
$CaCO_3 \Bumpeq 20\%$ CaO		1.95	5.13	Av. of 2 runs
$CaCO_3 \Bumpeq 10\%$ CaO		1.80	5.20	
Na_2CO_3	20	0.84	0.21	
Na_2CO_3	10	2.00	2.40	Av. of 2 runs
Na_2CO_3	5	1.72	3.40	Av. of 3 runs
Na_2CO_3	3	2.06	4.25	Av. of 3 runs
Na_2CO_3	1.5	2.39	5.26	Av. of 3 runs
Na_2CO_3	1.0	1.94	5.02	Av. of 2 runs
Na_2CO_3	0.5	1.61	5.32	Av. of 2 runs
Na_2SiO_3	1	1.78	4.87	
Na_2SiO_3	3	2.21	5.77	
MgO	5	1.57	5.22	
MgO	10	1.65	4.11	
		WHITE OAK		
......	..	1.17	4.91	Av. of 2 runs
Na_2CO_3	0.5	2.58	5.09	
Na_2CO_3	1.0	1.99	3.86	Av. of 2 runs
Na_2CO_3	1.5	2.47	3.40	
Fe_2O_3	10	1.16	3.78	
Fe_2O_3	5	1.08	4.37	
MgO	20	1.21	3.57	
MgO	5	1.14	2.77	
$MgCl_2$	10	0.49	..	
$MgCl_2$	20	0.36	..	

The results obtained with lime are very interesting in the large yields of wood alcohol obtained, but the greatly decreased yields of acid make the method unpromising.

CALCIUM CARBONATE—Several runs were made with calcium carbonate instead of calcium hydroxide in an attempt to maintain the high alcohol yields without decreasing the acid. With large amounts of calcium carbonate high yields of alcohol were obtained with only slightly decreased acid yields. With smaller amounts of carbonate the yields of acid were about normal while the alcohol yields were still increased to some extent. However, the amount of carbonate required to obtain satisfactory results was so great that the value of the charcoal was seriously diminished. Only in cases where the charcoal was not considered of much value or where it might be used as fuel in the near vicinity of the plant might this process be promising.

It might be supposed that the lime or carbonate was partly transformed into calcium acetate during the first part of the distillation and, if the temperature was not great enough to decompose it, a residue of calcium acetate might be left with the charcoal. This was tested out in several cases, but not more than a slight trace of calcium acetate was found in the charcoal.

SODIUM CARBONATE—The first few distillations with large amounts of sodium carbonate material were unsatisfactory. The distillations were rather violent at times and low yields of both alcohol and acid were obtained. This is shown in Table I, where the use of 20 per cent sodium carbonate gives very unpromising results. With 10 per cent, however, a slightly increased yield of alcohol was obtained, although the acid was still low. The amount of carbonate was gradually decreased, until with 1.5 per cent a large increase in alcohol was obtained without any decrease of acid. Smaller amounts of carbonate were not so satisfactory, although even with 1 per cent a considerable increase in alcohol was obtained. These effects of sodium carbonate on the reaction of the decomposition of wood by heat are difficult to explain, especially the frequent increase of acid yields due to an alkaline treatment. In several cases the charcoal was leached and the soluble salt examined. More than 20 per cent of the sodium was never found in the form of acetate, and this acetate never amounted to more than 0.3 per cent of acetic acid on the weight of the wood distilled.

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[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] THIS JOURNAL, **10** (1918), 264.

[3] H. P. Bassett, *Chem. Met. Eng.*, **20** (1919), 190.

[4] Hawley, THIS JOURNAL, **13** (1921), 301.

SODIUM SILICATE—Sodium silicate acts as a mild alkali similar to sodium carbonate. Similar results were obtained, although slightly larger amounts of silicate were apparently required to give the same increase in yields.

MAGNESIUM OXIDE—Magnesium oxide was used in concentrations of 5 and 10 per cent without appreciable increases in yields of either alcohol or acid.

White Oak Sawdust

All of these distillations were made with the same lot of sawdust from silver maple. The rest of the results reported in Table I were on white oak sawdust, and in comparing these with previous results it should be noted that the blank runs with oak where no chemical was used gave considerably lower yields, especially of alcohol. Sodium carbonate seems to have an even greater effect on the alcohol yields of oak than on those of maple. With as little as 0.5 per cent of sodium carbonate, one distillation gave double the yield of alcohol and slightly increased yields of acetate. The results obtained with 1 and 1.5 per cent were not so satisfactory, especially on account of the small acid yields, but high alcohol yields were obtained in both cases.

Iron oxide mixed with the sawdust in 5 and 10 per cent proportions did not show any promising results. The same was found in connection with the use of magnesium oxide and magnesium chloride. In the case of the latter chemical, high acid yields were recorded but tests showed that there was chloride present in this acid.

These results obtained with briquetted sawdust indicated that sodium carbonate was the most favorable chemical for further tests, both on account of its cheapness and its effect on the yields of alcohol. Further experiments were, therefore, carried out with this chemical upon wood in larger sizes.

Tests on Blocks of Wood

Blocks of white oak and maple wood 6 in. long were treated with a solution of sodium carbonate under 100 lbs. pressure so that a fairly uniform penetration of the solution was obtained. In the case of the maple blocks the distribution of the solution was especially complete. In the oak blocks, however, it was only the sapwood where penetration to the center was obtained, the heartwood showing only a slight penetration of perhaps 0.5 in. The blocks were distilled in the oil-jacketed retort in which previous wood distillation experiments have been made, and the results were compared with some of the same blocks which were distilled without previous chemical treatment. Table II shows the results of these distillations. In the case of the oak blocks a 50 per cent increase in wood alcohol was obtained with no decrease in the acetic acid in one series of runs (with 1.03 per cent carbonate), with a slight decrease in the other series (with 0.52 per cent carbonate). It is difficult to account for this decrease in acid where a smaller amount of sodium carbonate was used, but since all of the results given in the table were obtained from average figures on two distillations the results cannot be very inaccurate. In the case of the maple blocks there was a pronounced increase of alcohol (with 0.68 per cent and with 1.12 per cent carbonate), but in both series of runs the acetic acid was very considerably decreased. The question of the decrease in acid yields needs to be studied further since the results were erratic. In some distillations a slight increase appeared, while in other runs there was a very considerable decrease in acid.

TABLE II—BLOCKS OF WOOD TREATED WITH SODIUM CARBONATE

Sodium Carbonate	Treatment	Settled Tar	Dissolved Tar	Pyroligneous Acid	Charcoal	Gas	Total Tar	Acetic Acid	Wood Alcohol
Per cent		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
				OAK					
..	......	4.2	7.5	32.6	46.6	16.7	11.7	5.56	1.20
0.52	Pressure	5.1	5.5	32.5	42.5	20.0	10.5	4.71	1.85
1.03	Pressure	5.1	4.7	31.2	42.3	21.5	9.7	5.58	1.79
1.26	Soaked	5.2	6.7	32.1	43.4	19.4	11.9	5.66	1.40
				MAPLE					
..	......	5.0	9.0	38.8	38.7	17.5	14.0	7.65	1.67
0.68	Pressure	6.3	4.0	35.8	36.3	21.4	10.3	5.52	2.09
1.12	Pressure	6.7	8.2	38.8	38.9	15.7	14.7	6.74	2.16
3.15	Soaked	6.2	5.4	30.2	37.1	24.8	12.7	4.35	1.80

In order to show the effect of the sodium carbonate when not well distributed throughout the wood, runs were made on both oak and maple blocks which had simply been soaked in a solution of sodium carbonate without the application of pressure. The penetration was very slight at the ends of the blocks, and on the sides there was hardly more than a wet surface. The results of the distillation show that it is necessary to have all parts of the wood in contact with the chemical at the time of distillation in order to obtain the best results. Although in all cases there was a slight increase in alcohol from the soaked blocks, this increase was much less than in the case of pressure treated blocks or of briquetted sawdust.

The complete data on these runs with blocks are given in Table II, but little information of value can be obtained from the figures on the products other than acetic acid and wood alcohol. A variation in the relative amounts of pyroligneous acid, charcoal, and gas can be obtained by variation in the maximum temperature to which the charcoal is heated. Since this maximum temperature cannot be readily controlled in the apparatus used, the variations in these three products cannot be controlled and the percentage yield cannot be taken as an indication of the effect of the sodium carbonate.

Discussion of Application

It can be seen from these results that sodium carbonate previous to distillation can best be used in connection with processes for the distillation of sawdust. Since there are no processes of this kind in operation it has been impossible to test out the application of this principle on a commercial scale. It is very likely, however, that some sawdust distillation plants may be in operation in the near future.

It would probably be impossible to treat the ordinary distillation wood with sodium carbonate solution in such a way as to obtain much benefit therefrom. Most wood is distilled in 4-ft. lengths, and even with a pressure treatment it would be difficult to obtain an even distribution of the carbonate solution throughout such large sticks of wood. There are, however, a few commercial wood distillation plants which are using blocks because they are better suited for their artificial drying process than the ordinary 4-ft. sticks of wood. It is possible that these plants could submit their blocks to a pressure treatment with sodium carbonate solution before the wood goes to the driers and obtain thereby sufficiently increased yields of alcohol to make the process profitable. It is very likely that the value of the wood alcohol from wood distillation will be much greater than that of the acetic acid, so that any slight decrease in acid yield will not be a very great detriment to this process. If the commercial value of acetic acid products continues as low as it is at the present time, it is also possible that wood distillation plants will not attempt to recover acetic acid but will distil the alcohol from the pyroligneous acid and let the rest of the products go to waste. In this case the slightly diminished yields of acid would be of no disadvantage.

Other chemicals are being tested, and the effect of the distribution of the chemical is being determined. It is also hoped that an early opportunity will be afforded for trying out on a commercial scale the distillation of wood treated with sodium carbonate.

Effect of Change of Acidity upon the Rate of Diffusion of Tan Liquor into Gelatin Jelly[1,2]

By John Arthur Wilson and Erwin J. Kern

LABORATORIES OF A. F. GALLUN & SONS CO., MILWAUKEE, WISCONSIN

Thomas[3] has shown that the rate of diffusion of tanning extracts into gelatin jelly is usually greater the greater the ratio of nontannin to tannin in the extract. Thus for typical samples he found the rate of diffusion increasing in the order quebracho, hemlock bark, larch bark, oak bark, chestnut wood, gambier, sumac. This is also the order for decreasing astringency or rate of combination of hide and tanning material. The same order is roughly borne out in experiments dealing with the rate of diffusion into cowhide.

Our explanation of the fact that nontannins increase the rate of diffusion of the tannins into hide is as follows: Tannins and certain nontannins form compounds with the hide substance, but the hide-tannin compound is very stable, while the hide-nontannin compound is considerably dissociated. The nontannins, having a much smaller molecular weight than the tannins, diffuse more rapidly into the hide. When the slowly moving tannin reaches a point where it would combine with hide substance, it cannot do so because the point is already occupied by nontannin. Tannin that would otherwise have combined with hide substance near the surface of the hide is thus enabled to proceed into the interior and the measured rate of penetration is thereby increased. This action is more marked the greater the concentration of nontannin capable of combining with hide substance. The hide-tannin compound being much the more stable, tannin replaces nontannin as the hide-nontannin compound hydrolyzes.

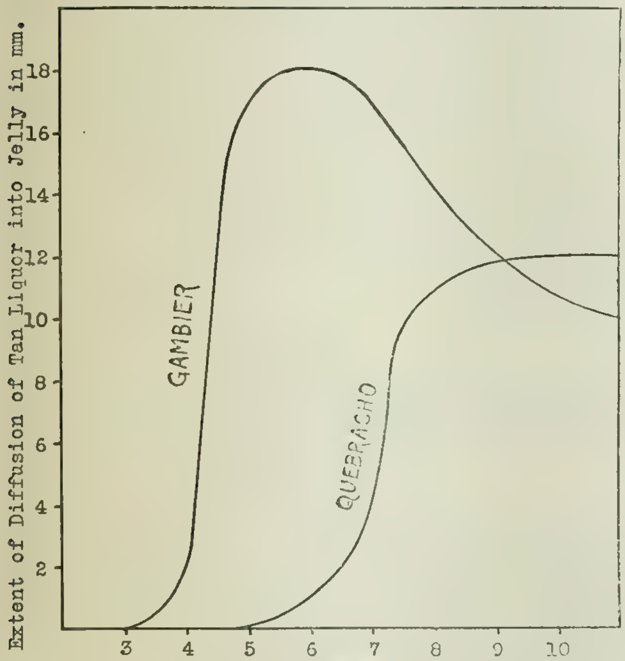

FIG. 1—SHOWING RATE OF DIFFUSION OF A TAN LIQUOR INTO GELATIN JELLY AS A FUNCTION OF THE HYDROGEN-ION CONCENTRATION

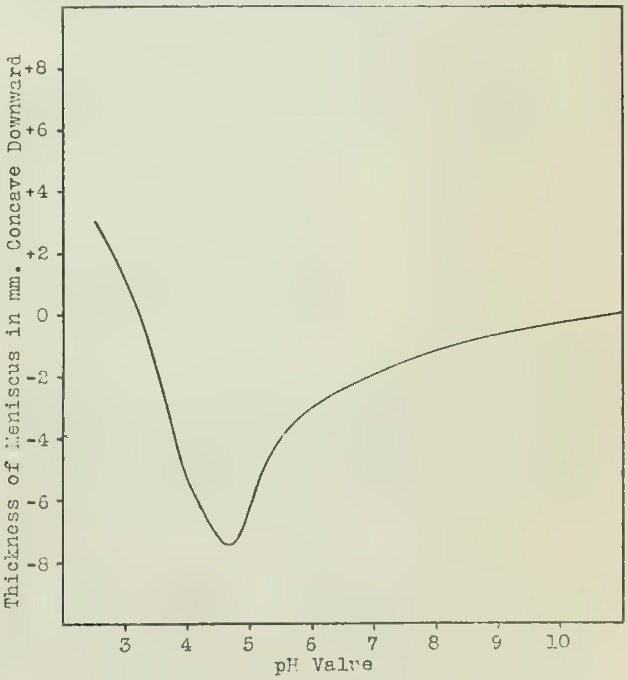

FIG. 2—INDICATING CHANGE OF SHAPE OF INTERFACE BETWEEN TAN LIQUOR AND GELATIN JELLY AS A FUNCTION OF THE HYDROGEN-ION CONCENTRATION

According to the Procter-Wilson theory[4] of vegetable tanning, the rate of tanning, and also of the combination of hide and certain nontannins, can be decreased either by increasing the electrolyte concentration or by lowering the positive electrical charge which hide substance possesses in acid solution, which can be accomplished by decreasing the acidity. We should therefore expect the constituents of a tan liquor, both tannin and nontannin, to penetrate hide substance more rapidly as the acidity of the tan liquor is decreased to the isoelectric point of hide substance.

Thomas prepared a 5 per cent dispersion of gelatin in hot water containing 0.1 per cent ferric chloride and poured it into a series of test tubes to three-quarters of their capacity. When the dispersions had set to jelly, equal volumes of solutions of different extracts were poured on top of the jellies, which were then placed in an ice box. All of the extract solutions were made to contain 1 per cent of dry solid matter. Tannin and some nontannins react with ferric chloride giving a dark blue or black color which served to indicate the extent of the penetration. In 96 hrs. the gambier had penetrated 18.0 mm., as against only 4.8 mm. by the quebracho. It was of course the extent of penetration by the nontannins that was measured, as these diffuse the more rapidly.

A large volume of a dispersion of gelatin in dilute ferric chloride solution was treated with tartaric acid until its pH value was reduced to 2.5, as determined by the hydrogen electrode. Equal portions were then treated with sodium hydroxide to give the desired pH values, which ranged from 2.5 to 11.0. Dilutions were such that the final dispersions contained 5 per cent of gelatin and 0.1 per cent of ferric chloride, as in the experiments of Thomas.

Gambier and quebracho extracts were selected for the test which showed by analysis:

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[1] Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York City, September 6 to 10, 1921.

[2] Received August 15, 1921.

[3] *J. Am. Leather Chem. Assn.*, **15** (1920), 593.

[4] *J. Chem. Soc.*, **109** (1916), 1327.

	Gambier Per cent	Quebracho Per cent
Water	48.84	19.41
Insoluble	7.58	9.50
Nontannin	36.14	27.06
Tannin[1]	7.44	44.03

[1] Wilson-Kern method, THIS JOURNAL, **12** (1920), 465.

Solutions of these extracts were treated with tartaric acid to give a pH value of 2.5. Equal portions were then treated with sodium hydroxide to give a series of pH values the same as in the series of jellies. Each final liquor contained 1 g. of dry solids of the original extract per 100 cc.

The gelatin dispersions were poured into test tubes and allowed to set. On each was poured a given volume of tan liquor having the same pH value as the jelly. Both the quebracho and gambier series were run in duplicate. They were kept in the ice box and examined at intervals for 96 hrs.

The extent of the diffusion of the tan liquors into the jellies is shown in Fig. 1, the measurements being taken after 96 hrs. In each case the duplicate series were practically identical.

Gambier, which has a high ratio of nontannin to tannin, begins to penetrate at a pH value of 3.0 and reaches its maximum rate at pH=6.0. Quebracho, on the other hand, scarcely shows any penetration until pH=4.7, the isoelectric point of gelatin, is reached. At pH values greater than 9, however, the quebracho liquor penetrates at the greater rate, possibly because of its higher tannin content.

An interesting observation made during these experiments was that the shape of the interface between tan liquor and jelly also changes with the pH value. At pH=2.5 it was concave downward, at pH=3.0 it was flat, but with increasing pH value it became concave upward with the thickness of the meniscus increasing to a maximum of 7.5 mm. at pH=4.7 and then decreasing until the interface again became flat at pH=11.0. The thickness of the meniscus as a function of the pH value is shown in Fig. 2. This change in shape of the interface appears to be related to the swelling of gelatin. The point of minimum in the curve in Fig. 2 occurs at the isoelectric point of gelatin, pH=4.7, while the curve slopes upward towards the points of maximum swelling of gelatin, pH=2.4 and pH=11.7, for the external solution. The measurements recorded are those for the gambier series, but the quebracho series showed practically the same effect.

Studies have also been made of the effect of change of acidity upon the rate of diffusion of tan liquors into cowhide. With increasing pH values up to about 8 there is a distinct increase in rate of diffusion, but because of the flaccid nature of hide at pH=8 it is difficult to make accurate measurements of the rate of diffusion. At pH values below 3 and above 11 the hide swells considerably and becomes rubbery and distorted.

SUMMARY

As ordinarily used in tanning, gambier and quebracho extracts show marked differences in the rate of tanning and of penetration into the hide. It is shown that the rate of penetration is a function of the hydrogen-ion concentration as well as of the nontannin content. The shape of the interface between a tan liquor and gelatin jelly was found also to be a function of the hydrogen-ion concentration.

The Electrometric Titration of Azo Dyes[1]

By **D. O. Jones** and **H. R. Lee**

THE NEWPORT CO., CARROLLVILLE, WISCONSIN

Electrometric methods of analysis have, in recent years, come into quite general use, particularly in the field of inorganic chemistry. Titanous chloride, originally suggested by Knecht[2] as a reagent for the estimation of a large number of compounds, both organic and inorganic, has also in recent years found increased application, particularly in the field of dye chemistry.[3]

Titanous chloride, combined with the electrometric method for determining the end-point of the titration, has been successfully applied in this laboratory to the analysis of azo dyes. The indirect titration was used in practically all analyses of azo dyes and nitro bodies. The reduction was made with an excess of standard titanous chloride and the excess was determined by titration with ferric alum.

In the former titanous chloride methods, involving the use of a thiocyanate indicator, the end-point was sometimes difficult to determine with accuracy on account of the turbidity of the solution, the presence of insoluble reduction products, or the masking of the end-point by the color of the solution itself. Thiocyanate was not satisfactory as an outside indicator, because the titrations were carried out in an atmosphere of carbon dioxide and because the solutions themselves were often of a pink color.

The reduction products of some azo dyes produce, with ferric salts, characteristic colors, which sometimes furnished indications of the end-point.[4] For example, diamino-H-acid gave a blue color and amino-naphthionic acid a green color with ferric salts. These colors are not as a rule alike under all conditions and seldom furnish an accurate means of determining the end-point.

STANDARD SOLUTIONS

A 0.25 *N* $TiCl_3$ solution has been adopted for the analysis of azo dyes and a 0.05 *N* ferric alum solution for the back titration. The methods of preparing, storing and using the solutions were in general those of Knecht and Hibbert[5] with modifications similar in general to those of English.[6] LaMotte's titanous chloride was used in preparing the solutions and the boiling in the preparation was omitted.[7]

APPARATUS

For the application of the electrometric method to oxidimetric reactions, reference is made to the work of Hostetter and Roberts.[8] Wendt's electrotitration apparatus, with slight modifications in the calomel half cell and the addition of a reversing switch, was used in this work. Any modifications in the electrometric apparatus in its application to oxidimetric reactions as published by Roberts[9] will also find application here.

The electrometric apparatus used in conjunction with titanous chloride is shown in the accompanying diagram. Carbon dioxide from a drum was used for maintaining an oxygen-free atmosphere in the reaction flask, which consisted of a 250-cc. Pyrex extraction flask with a 3-hole rubber stopper. Two holes were for the platinum electrode and capillary tube of the calomel half cell, respectively, and the third for admitting the buret. In recent practice, the calomel half cell remained clamped to a ring stand in preference to the arrangement shown in the diagram. Contact was made to a separate capillary tube in the flask by means of three-sixteenths inch rubber tubing which constituted a salt bridge. A small calomel half cell, similar to the one used by Hostetter and Roberts[10] and attached directly to the reaction flask, was also satisfactory.

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[1] Presented before the Division of Dye Chemistry at the 62nd Meeting of the American Chemical Society, New York, September 6 to 10, 1921.

[2] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," **1918**.

[3] F. English, THIS JOURNAL, **12** (1920), 994.

[4] Arthur H. Green, "Analysis of Dyestuffs," 2nd Ed., 117.

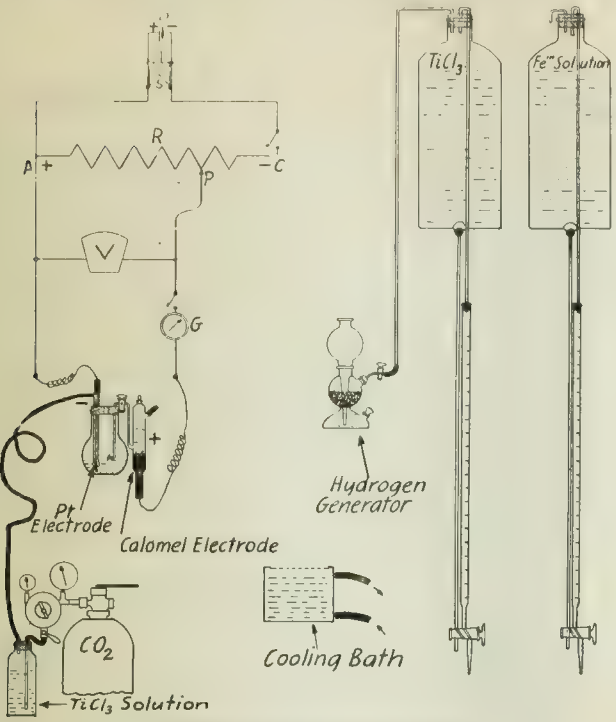
[5] *Loc. cit.*

[6] *Loc. cit.*

[7] *J. Am. Chem. Soc.*, **43** (1921), 91.

[8] *Ibid.*, **41** (1919), 1337.

[9] *Ibid.*, **41** (1919), 1358.



Electrometric Titration Apparatus

Standardization of $TiCl_3$

The work of English[11] shows that results 0.4 per cent higher than theoretical were obtained for a pure nitro compound, based on standardization of the titanous chloride by ferrous ammonium sulfate.

A fresh sample of Baker's analyzed ferrous ammonium sulfate was carefully oxidized with potassium permanganate and used in standardizing a 0.25 *N* $TiCl_3$ solution. Analyses of *p*-nitroaniline were made with this titanous chloride and by the sodium nitrite method. All steps in the standardization with ferrous ammonium sulfate and in the analyses of *p*-nitroaniline were alike with respect to time of expelling air, boiling, cooling, volume of solution, etc. Table I shows analyses of *p*-nitroaniline by the two methods.

Table I

Sample	With $TiCl_3$ Per cent	With $NaNO_2$ Per cent
I	99.67	99.55
	99.75	99.55
Average	99.71	99.55
II	99.02	99.11
	98.95	99.08
Average	98.98	99.09

The analyses by sodium nitrite were made at different times with different standard solutions. Compared with the results by sodium nitrite, ferrous ammonium sulfate and *p*-nitroaniline are equally good standards when used under the same conditions.

Fifty cc. of stock solution of *p*-nitroaniline containing 4 g. per liter were used for each standardization. Sublimed *m*-nitroaniline was also found satisfactory as a standard.

Analytical Procedure

Weigh a sample of the finely powdered dye, approximately 1 g. and seldom less than 0.5 g., sufficient in quantity to require for reduction 30 to 45 cc. of 0.25 *N* titanous chloride. Transfer the sample, which is usually in the form of the soda salt, to the reaction flask, add 25 cc. distilled water, cover loosely, and place the flask on a steam bath for about 10 min. to dissolve or at least soften the particles. Add 25 cc. of 40 per cent sulfuric acid, stopper the flask, and pass a current of CO_2 through for 5 min.; then add the required amount (35 to 50 cc.) of titanous chloride (at least 5 cc. 0.25 *N* $TiCl_3$ in excess of that required for reduction are added). Boil for 5 min. and cool to 30° C. in a bath of running water. Titrate back the excess of titanous chloride with ferric alum. The titration is made in approximately the same volume as in the standardization.

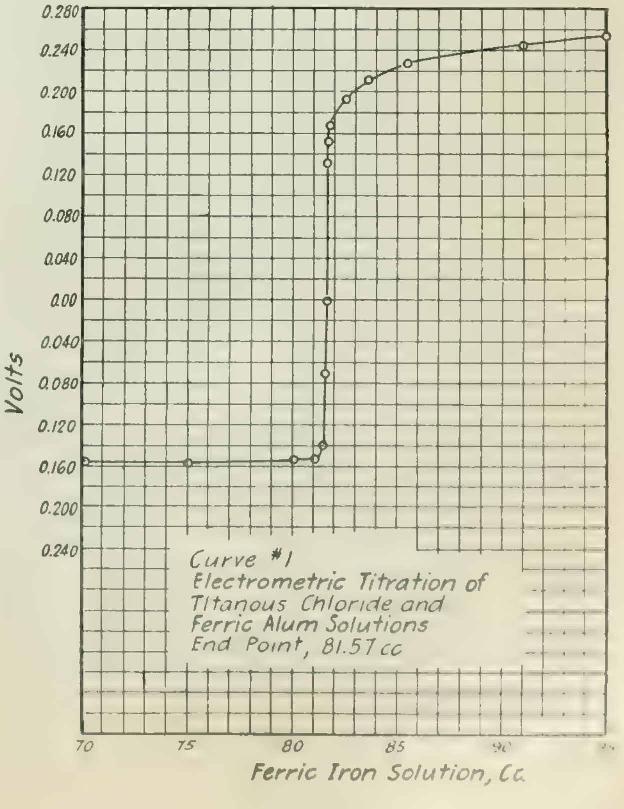
The back titration is conducted as follows: Adjust the potentiometer and read voltages for each addition of ferric alum. Add the latter at first in 5-cc. portions, gradually decreasing to 0.1 cc. or less. When passing over the end-point, reverse the poles in the usual manner and again read voltages as additions of ferric alum become larger.

Plot volts as ordinates against cc. ferric alum solution as abscissas and determine the end-point from the curve. From this the quantity of titanous chloride consumed is readily obtained.

For routine analysis, practically all azo dyes can be analyzed with sufficient accuracy without reading the voltmeter or plotting a curve. Adjust the potentiometer at the beginning of the back titration, until, on closing the circuit, the galvanometer shows no deflection. At the end-point a permanent large swing of the galvanometer is obtained.

Interpretation of Curves

Curves 1 and 2 are typical of those obtained in the determination of the relative strengths of the solutions and in the standardization with *p*-nitroaniline, respectively. The end-points cannot be mistaken by as much as 0.10 cc. of 0.05 *N* ferric alum, which, in terms of 0.25 *N* titanous chloride, in-



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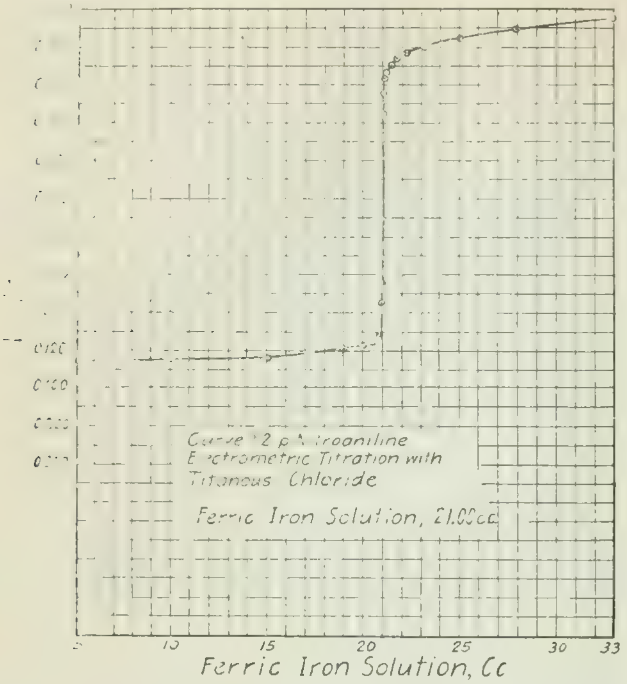
[10] *Loc. cit.*, 1340.

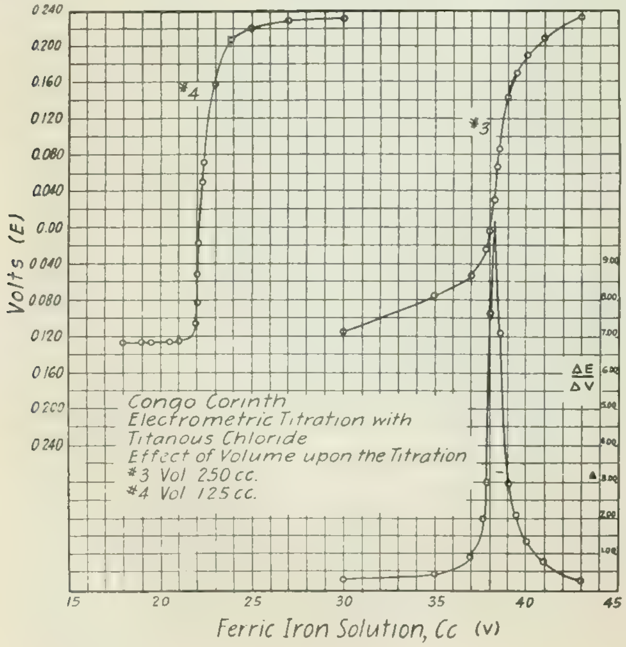
[11] *Loc. cit.*, 995.

troduces as error less than 0.05 per cent in the analysis. Curves 3 and 4 were obtained with Congo Corinth. Curve 4 is typical of those obtained in the most improved practice and was obtained using a 1.0 g. sample, 0.25 *N* titanous chloride, and a volume at the end-point of 125 cc. Curve 3 was obtained with 0.15 *N* titanous chloride, a 0.5 g. sample, and a volume of 250 cc. Curves with different slopes, obtained under different conditions, have in all cases indicated the same end-point with sufficient accuracy.



In Curve 3 is shown the application of the method used by Hostetter and Roberts[12] in which the coincidence of the curves, obtained by plotting $\Delta E/\Delta V$ against V, indicates the true end-point.

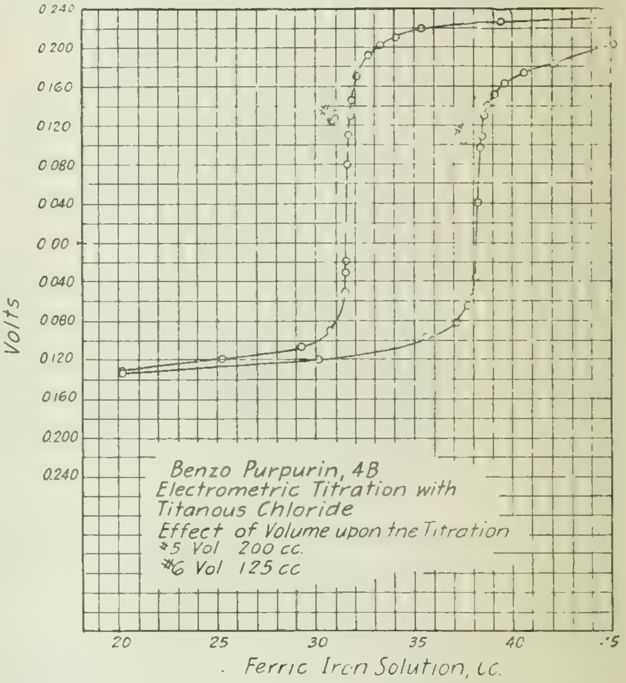
Curves 5 and 6, typical of Benzo Purpurine 4B, show again a slight difference in favor of Curve 6 with the smaller volume. Curve 5 was obtained with 0.15 *N* titanous chloride and a 0.5 g. sample; Curve 6 with a 1.0 g. sample and 0.25 *N* titanous chloride. The back titration in both cases was made with 0.05 *N* ferric alum.



DISCUSSION

The work of Callan, Henderson and Strafford[13] shows that low results obtained in the analysis of some nitro compounds with titanous chloride can be traced to the formation of chlorinated amines during the reduction. They have overcome this difficulty by substituting titanous sulfate for the chloride. No difficulties of this nature were encountered in applying the titanous chloride method to the analysis of azo dyes. However, since the electrometric titration with titanous chloride is subject to any limitations of titanous chloride itself, the sulfate can no doubt be substituted here as well, in applying the method to a larger number of compounds.

Titrations of titanous chloride with ferric alum by the electrometric galvanometer deflection method, in which thiocyanate was present in the solution, have shown that 0.03 cc. 0.05 *N* ferric alum solution was sufficient to give the galvanometer pointer a decided and permanent swing and at the same time to change the solution from colorless to a decided pink.



The electrometric titration is valuable as a means of accurately analyzing a larger number of azo dyes for the control of process yields than could be accomplished by previous methods.

SUMMARY

1—The difficulties encountered in the analysis of azo dyes with titanous chloride by previous methods are enumerated.

2—An analytical procedure is described whereby the electrometric method of following oxidimetric reactions is used in conjunction with titanous chloride for the successful analysis of azo dyes and nitro compounds.

3—A modified electrometric apparatus adapted for use with titanous chloride is described.

4—Typical curves for obtaining the end-point are shown.

ACKNOWLEDGMENT

Acknowledgment is made to Mr. E. V. Romain of this laboratory for assistance in obtaining data in the development of this paper.

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[12] *Loc. cit.*, 1341.

[13] *J. Soc. Chem. Ind.*, **39** (1920), 86*t*.

Comparison of the Various Corn Products Starches as Shown by the Bingham-Greene Plastometer[1]

By Chr. E. G. Porst and M. Moskowitz

Research Laboratory, Corn Products Refining Co., Edgewater, New Jersey

Up to the present the method of determining the flow characteristics of starch and dextrin pastes was the so-called fluidity test, described in the original communication by H. Buel.[2] The fluidity funnel is simply a 4-in. glass funnel with a stem drawn to a point so that if 125 cc. of water are poured into the funnel 105 cc. run out in 70 sec. The different funnels are of only approximately the same dimensions and are calibrated in terms of one of the funnels for pastes made of 5 and 7.5 g. of starch. For starches of low fluidity, 5 g. of starch are stirred with 10 cc. of water, 90 cc. of 1 per cent caustic soda solution are added, and the mixture is stirred for 3 min. and allowed to stand 0.5 hr. The cc. flowing in 70 sec., corrected to the standard funnel, give the fluidity term as used above. The thin boiling starches are sold on the fluidity specifications—2 F should give a 20 fluidity, 9 F a 90 fluidity within practical limits. This method, of course, is not scientific and, although it is good as a control, does not enable all the characteristics of a paste to be studied, especially at the concentrations used in practice.

In order to investigate the physical characteristics of starches, gums, and dextrins, Carl Bergquist, chemist of this company, worked in conjunction with the Bureau of Standards on this investigation. This paper is a continuation of the investigations carried on by Herschel and Bergquist,[3] and for the theory involved and the description of the apparatus used reference should be made to the original paper. Herschel and Bergquist have found that viscosity or plasticity plays a very important part in the practical application of starch and dextrin pastes, together with their chemical composition and concentration. The present investigators have endeavored to obtain such results as would enable the starch users to know the particular properties of the different grades of corn starches manufactured. This would facilitate matching of products used for a particular purpose.

It will only be necessary to define a few of the terms and empirical equations used. With viscous substances the flow through capillary tubes (neglecting the correction for kinetic energy and the correction for the resistance outside the capillary) is Poiseuille's formula

$$n = \frac{\pi g r^4 p t}{8 v l}$$

where n = viscosity in c. g. s. units, poises.
g = acceleration of gravity = 981 cm. per sec.^{2}
r = radius of capillary in cm.
p = pressure in g. per sq. cm.
t = time of flow in sec.
v = volume of flow in cc.
l = length of capillary in cm.

or the fluidity is $= \frac{1}{n} = \frac{8l}{\pi g r^4} \frac{V}{pt}$.

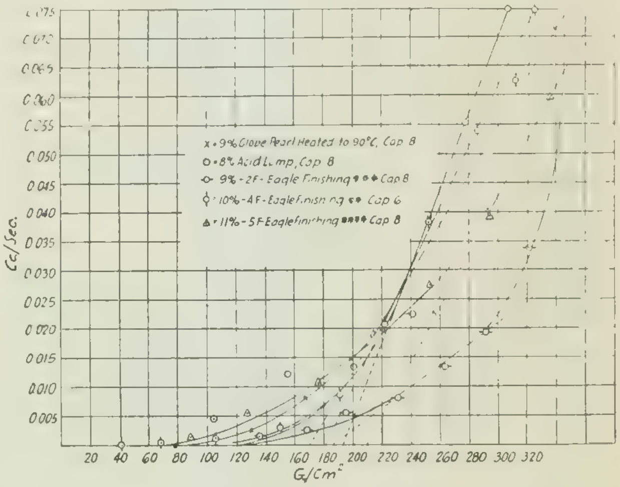
Where $\frac{8l}{\pi g r^4}$ is a constant, K, for a given capillary, K can be determined by calculation from the dimensions or by direct determination with a heavy oil of known viscosity.

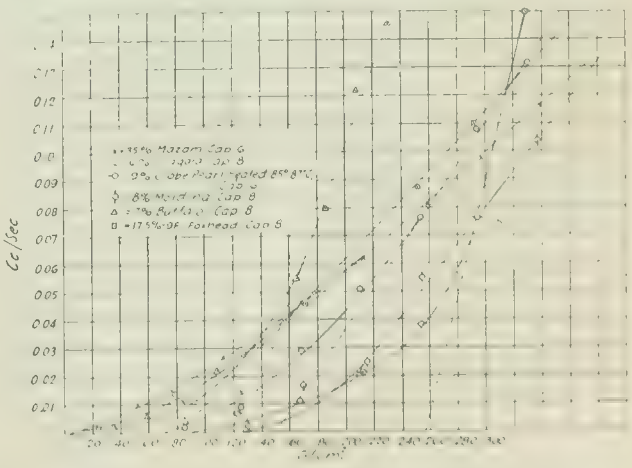
The flow for viscous materials, therefore, is proportional to the pressure. With plastic substances there is no flow until the pressure or shearing force has exceeded a certain definite value. The terms used with these materials are rigidity, R, and mobility instead of viscosity and fluidity.

$$\text{Mobility} = \frac{1}{R} = \frac{KQ}{p-f}$$

where f is the intercept of the asymptotes or tangent to the curve with the pressure axis. The term f in c. g. s. units is called by Bingham "yield shear value."[4]

The apparatus and method of procedure were the same as described in the article by Herschel and Bergquist. In order to be able to duplicate results the method of making pastes was kept as uniform as possible. A mechanical stirring arrangement which rotated at about 12 r. p. m. was used. This eliminated as far as possible variations due to changes in the rate of stirring. This mixing was not sufficient to keep the starch suspended until gelatinization was completed. However, since it was not desirable to increase the rate of stirring after the paste was gelatinized, a fairly slow stream of inert gas was bubbled through hot water and brought into the bottom of the paste kettle in the early stages of the paste making. When gelatinization had taken place the stream of gas was shut off and only mechanical stirring continued. The whole was enclosed with a loosely fitting cover. There was very little variation in concentration of the pastes made by this method. For each test 600 g. of paste were made up. During the heating the temperature in the paste container was observed. It will subsequently be observed from the





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[1] Presented before the Section of Sugar Chemistry and Technology at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] *8th Internat. Cong. of Applied Chem.*, XIII, 63.

[3] This Journal, **13** (1921), 703.

[4] Bureau of Standards, *Scientific Paper* **278**.

TABLE I—PLASTOMETER RESULTS

Description of Starch Sample	Paste Per cent Dry Substance	Temperature to Which Paste Was Heated ° C.	Consistency of Cold Paste	Capillary 6				Capillary 8			
				Yield G. per Sq. Cm.	Dynes per Sq. Cm.	Mobility	Rigidity $\frac{1}{\text{Mobility}}$	Yield G. per Sq. Cm.	Dynes per Sq. Cm.	Mobility	Rigidity $\frac{1}{\text{Mobility}}$
				Thick Boiling Starches							
Globe Pearl	7	87	Sloppy—fractures	76	74,600	1.530	0.665	167	164,000	4.67	0.214
	8	90–95	Firm -fractures	221	216,800	0.153	6.54	260	255,000	0.152	6.58
	9	85–87	Firm (weaker than 8 per cent)—fractures	257	252,000	0.494	2.02	255	250,000	0.306	3.25
	8	85	Slightly weak—fractures	106	103,900	0.490	2.04	101	99,000	0.353	2.83
	9	85	Slightly weak—fractures	164	161,000	0.482	2.07	170	166,500	0.428	2.33
Special Molding	7	85	Sloppy—fractures	85	83,400	1.129	0.886	146	143,000	2.236	0.448
	8	85	Weak—fractures	116	113,800	0.385	2.58	176	172,500	0.664	1.51
	9	87	Firm—fractures	210	206,000	0.368	2.72	265	260,000	0.283	3.53
Buffalo	7	85	Slightly weak—fractures	120	117,800	1.600	0.625	126	123,300	1.390	0.720
	8	85	Good—fractures	232	227,600	1.158	0.864	254	249,000	1.435	0.697
	9	85	Good—fractures	250	245,000	0.673	1.48	Flow too slow			
Acid Lump	6	86	Weak—fractures	94	92,100	2.63	0.380	96	94,000	1.31	0.764
	7	85	Weak—fractures	76	74,500	0.870	1.15	93	91,200	0.473	2.11
	8	85	Weak—fractures	135	132,200	0.596	1.68	194	190,000	0.683	1.48
	9	86	Firm—fractures	180	176,500	0.543	1.84	241	236,000	0.766	1.30
Niagara	6	85	Fair—fractures	125	122,500	0.701	1.43	151	148,000	0.759	1.32
	7	85	Firm—fractures	160	157,000	0.355	2.82	192	188,200	0.307	3.76
	8	85	Very firm—fractures	265	260,000	0.0520	19.20	226	221,600	0.0443	22.50
				Thin Boiling Starches							
2 F Eagle Finishing ***	8	90	Weak—fractures	121	118,500	0.492	2.03	170	166,800	0.597	1.63
	9	87	Good—fractures	154	151,000	0.249	4.01	186	182,200	0.192	5.20
	10	90	Good—fractures evenly	172	168,500	0.0323	30.9	201	197,000	0.0266	37.60
4 F Eagle Finishing**	9	85	Weak—fractures	115	112,800	0.474	2.11	127	124,200	0.820	1.22
	10	87	Good—fractures	181	177,200	0.134	7.46	184	180,500	0.105	9.52
	11	86	Good—fractures	183	179,500	0 0876	11.40	209	205,000	0.043	23.20
	12	90	Good—fractures	197	193,000	0.00880	113.80	...	.....	.....	.....
5 F Eagle Finishing****	11	85	Weak—fractures	185	181,500	0.725	1.38	210	206,000	0.483	2.06
	12.5	87	Weak—fractures	207	203,000	0.124	8.06	272	266,200	0.149	6.72
	15	85	Firm—fractures	225	221,000	0.0119	88.00	...	.....	.....	.....
7 F Eagle Finishing*	15	85	Weak—no fracture, good spreading qualities	213	209,000	0.543	1.84	230	225,600	0.256	3.91
	17.5	90	Weak—no fracture Smooth	207	203,000	0.270	3.71	235	230,400	0.214	4.67
	20	85	Fair—no fracture	231	227,000	0.0123	81.30	...	.....	.....	.....
	22.5	90	Fair—no fracture smooth —good spreading qualities	230	226,000	0.00436	230.40	...	.....	.....	.....
9 F Foxhead	17.5	85–87	Fairly fluid—very smooth	60	58,800	0.595	1.68	83	81,400	0.543	1.84
	20	87–90	Weak—very smooth (no fracture)	93	91,100	0.236	4.24	120	117,500	0.188	5.32
	22.5	87	Fair—very good spreading qualities	92	90,000	0.101	9.90	96	94,200	0.056	17.80
	25	87	Weak—very good spreading qualities	131	128,500	0.0720	13.90	171	167,500	0.0575	17.40
	27.5	87	Little weak—very good spreading qualities	177	173,500	0.0116	86.200	177	173,500	0.00810	123.50
	30	85	Fair—very good spreading power	196	192,000	0.00285	351.00	...	.....	.....	.....
	32.5	85–87	Fair consistency—no fracture—good spreading qualities	207	203,000	0.000883	1131.00	...	.....	.....	.....
				Mazam							
	35	95	Fairly fluid	82	80,400	0.506	1.98	69	67,600	0.442	2.26

data that, in order to get results comparable one with another, it is very important to have the final temperature the same for all the starch pastes. After the 0.5-hr. heating at 85° C. or other temperatures as noted, the pastes were poured through cheese-cloth to remove any lumps which might clog the capillaries, and allowed to cool down slowly to 25° C. until the next day. The upper layer of paste was rejected. Conditions for the treatment of successive samples still need to be made more uniform.

The capillaries were measured by the Bureau of Standards. The constant K used for investigations was the one obtained by determining the constant $K = \frac{p}{Qn}$ from determinations on castor oil, the viscosity of which was measured by the Bureau of Standards. In the equation the dimension r^4 is used, so that a very small error in r can cause quite a large error in the constant.

No. of Capillary	Length in Cm.	Diameter of Minor Axis	Diameter of Major Axis	Calculated Diameter	Calculated Constant K	Constant Determined with Standardized Castor Oil	$\frac{1}{d}$
6	2.62	0.146	0.152	0.149	221.4	256.5	17.5
8	3.01	0.105	0.108	0.106	972.9	1025.	28.3

EXPERIMENTAL RESULTS

Table I gives a summary of the results on eleven starch products. The first five are the thick boiling starches, the next five are the thin boiling starches, and the last, Mazam, a partly dextrinized starch containing 4 to 6 per cent of reducing sugars. The column "consistency of cold paste" gives the molding quality of the paste.

The sets of curves give the experimental results of a certain concentration of each starch on the two capillaries used. In making the tests, about three concentrations were tested that would come within the upper and lower limits for best flow through the plastometer. Since starch users have been accustomed to the term fluidity, the values of the mobilities were included in the tabulation.

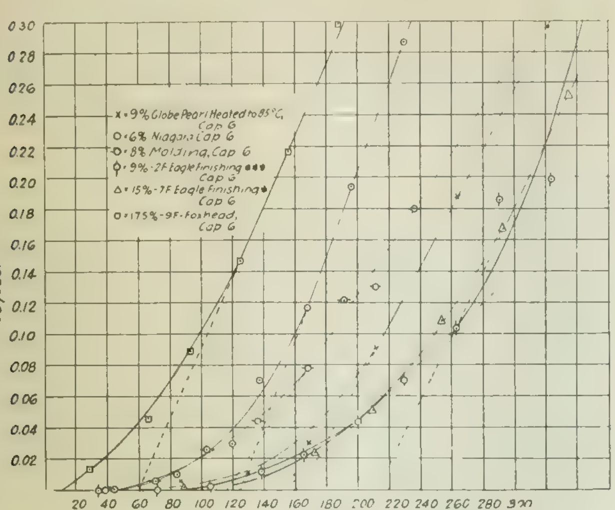
The chemical differences of the ten starches are given in Table II.

TABLE II

No.	Name of Starch	Moisture Per cent	Acidity Per cent	Alkalinity Per cent	Soluble Per cent	Protein Per cent	Fluidity
1	Globe Pearl.......	10.38	0.06	..	0.09	0.54	..
2	Buffalo...........	10.45	0.09	..	0.20	0.47	..
3	Special Molding ..	10.92	0.07	..	0.35	0.46	..
4	Acid Lump.......	11.68	0.08	..	0.22	0.43	..
5	Niagara...........	11.61	..	0.04	0.62	0.56	..
6	2 F Eagle Fin.***.	11.83	0.07	..	0.33	0.40	22.5
7	4 F Eagle Fin.** .	9.98	0.07	..	.34	0.43	46.0
8	5 F Eagle Fin.****	10 10	0.08	..	.84	0.44	57.5
9	7 F Eagle Fin.* ..	10.15	0.08	..	2.19	0.40	71.5
10	9 F Foxhead......	9.85	0.10	..	1.25	0.47	94.0
11	Mazam..........	8.16	..	..	99.0	..	

GLOBE PEARL STARCH—The variations in the results obtained are attributable to the fact that the final temperature to which the paste was heated varied to some extent. Two samples of pastes of 8 per cent on dry substance were made up in identically the same way except that one was heated to 90° to 95° C., the other to 85° only. The paste obtained from the 90° temperature was very firm, giving a yield value with capillary 6 of 221 g. per sq. cm. and a mobility of 0.153.

The 8 per cent paste kept at 85° C. had a yield value of 106 g. per sq. cm. and a mobility of 0.490. Its consistency was weak. A 9 per cent concentration heated to 87° gave a slightly higher yield value than the 8 per cent heated only to 85° C. The mobility of this 9 per cent paste was almost three times as high as that of the 8 per cent heated to 90° C., which under normal conditions should have been reversed. These variations really existed in the pastes because the 9 per cent paste was much weaker than the 8 per cent. The determined dry substance on these pastes checked the concentrations given. A 9 per cent paste heated to 85° C. gave a lower yield and about the same mobility as the 9 per cent heated to 87° C. However, the 9 per cent paste heated to 85° gave a higher yield value than the 8 per cent paste heated to 85° C., which is consistent. Both pastes heated to 85° C. were weak. Globe Pearl pastes of this concentration should give firm pastes and evidently it may be best to heat these pastes to 90° C. rather than to 85° so as to make sure that gelatinization is complete. This slowness of gelatinization is noticed with some materials more than with others. The character of the curves is regular, the flow being directly proportional to the increase of pressure (at the higher pressures).



BUFFALO STARCH—The curves are very consistent, being typical plastic flow curves. Even when the yield value is high, the mobility is also comparatively high.

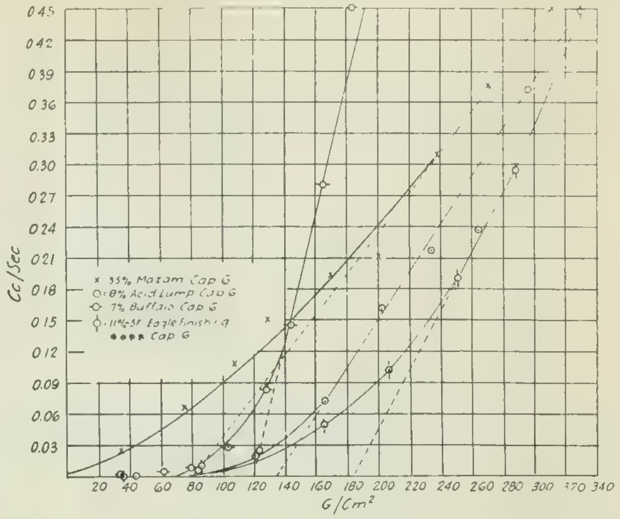
SPECIAL MOLDING STARCH—Gives fairly regular curves.

ACID LUMP STARCH—The curves are regular plastic flow curves. Results are consistent.

All of the acid starches give mobilities that are from 2.00 to 0.300, depending on the concentration. The mobilities as determined by the two capillaries seldom check, usually being lower with the smaller capillary, sometimes only one-half of the value obtained with the larger capillary.

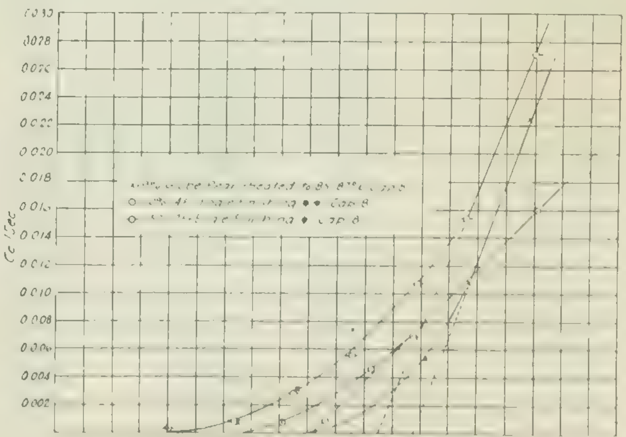
NIAGARA STARCH (a slightly alkaline starch)—The curves are very good type curves, the flow at higher pressures being directly proportional to the increase of pressure. The mobilities in the 3 cases for the 2 different capillaries check almost within experimental error. The mobilities go to 0.05 on the 8 per cent concentration. The yields are much higher than corresponding concentrations of 8 per cent acid starches.

THIN BOILING STARCHES—The characteristics of 7 F and 9 F were much different from those of the other starches. They never became firm enough to give a fracture similar to the other starches. 9 F especially gives a smooth uniform paste of very good spreading power. 2 F gives a very firm paste with 9 per cent concentration, 4 F with 11 per cent, 5 F with 15 per cent, 7 F pastes become fair in consistency at 20 per cent concentration but never firm; 9 F becomes fair with 22.5 per cent concentration and remains a smooth uniform paste even up to 35 per cent. With 7 F starch the yield values remain about the same at the different concentrations, about 220 g. per sq. cm. The mobilities of higher concentrations of 7 F and 9 F are very low, 0.0123 to 0.00436 for 7 F and 0.00285 to 0.000883 for 9 F, showing that pastes have a very good body and excellent covering power, and will not flow easily. The characteristics of the more modified thin boiling starches make them very desirable for sizing purposes, on account of the large concentrations in which they can be used and other characteristics such as low mobility and fairly high yield value.



Yield values for the different thin boiling starches are higher for the smaller capillaries. The mobilities are lower for the smaller capillary, sometimes checking to within experimental error and sometimes one-half as large.

The thin boiling starches give results that make it difficult to obtain the yield and mobility values, because even at the highest pressures the increase of flow appears to be some function of the pressure. Comparison of these starches will have to be made with the use of other mathematical equations. When some of these curves were plotted on logarithmic paper, even the lower points fell into a single straight line, showing that the flow is some function of the pressure even at the lower pressures. Herschel and Bergquist point out that a slight difference in weighting of points will cause a great variation in the yield and that in reality nearly all points were on the curved part of the graph. They claim there is a lack of accurate formulas. The same was found



true with these results. In most cases different possibilities were weighted and the most logical values taken. These are believed to be approximately correct.

Conclusion

In general the plastometer has given very interesting data. It has many times enabled the laboratory to advise exactly what product will satisfy a particular requirement. Also, it has been used in conjunction with the chemical analysis to tell what product would exactly match a submitted product. Some of the data obtained indicated that the empirical formulas of the first degree as used at present will have to be modified. Investigation will also have to be carried further as to the effect of final temperature to which the pastes are heated as well as the effect of different ingredients on the starches.

The Tyndallmeter Reading of Soil Dispersoids[1]

PRELIMINARY REPORT

By F. M. Scales and Franklin W. Marsh

Office of Soil Bacteriology Investigations, Bureau of Plant Industry, U. S. Department of Agriculture, Washington, D. C.

The work herein reported was performed to obtain supplementary data for a bacteriological investigation so that we might gain a better knowledge of the conditions under which the bacterial flora of the soils was maintained. A complete report will be published in the near future.

Investigators have in the past made determinations of the dispersoid content of soils by the water-vapor adsorption, dye or gas adsorption, and suspension methods. The first two usually require a modification of procedure for each soil type and on this account are not well adapted for the study of a variety of soils. The suspension method gives the most promise and, if a satisfactory procedure can be developed, ought to yield fairly close results.

In this investigation a suspension method was employed in order to obtain a measure of the concentration of the disperse phase in a soil by means of a Tyndallmeter. The suspensions from the naturally moist soils were examined for dispersoid content after they had stood for 24 hrs. No attempt was made to determine the size of the organic or inorganic particles in the disperse system but, if it is assumed that the size of the particles left in suspension after 24 hrs.' settling was approximately the same for the different soils, the strength of the Tyndall beam may be taken as roughly proportional to the concentration of dispersed material.[2]

In any case, since all the suspensions were prepared by a uniform procedure, the factors obtained bear sufficient relation to each other to furnish a good index of the comparative concentrations of the small particles which may be important factors in the maintenance of soil fertility.

Apparatus

In 1919 Tolman and Vliet[3] published a description of an apparatus which they had perfected for measuring the strength of the Tyndall beam produced by suspensions, colloidal solutions, smokes, and mists. The specifications for the Tyndallmeter may be found in the publication referred to. The apparatus with the equipment necessary for its operation is shown in the figure.

The Tyndallmeter is designated by the letter A on its triangular support. Readings are made with the apparatus by inserting the suspension in its container in the chamber B, and examining it through the eyepiece of the Macbeth illuminometer just above. The illuminometer is connected by wires with the milammeter C, which in turn is connected with the three dry cells. The lamp which furnishes the light for the Tyndall beam is at the lower end, D, of the Tyndallmeter and is connected by a wire with the positive pole of the storage battery E. The negative pole of this battery is connected with the carbon compression rheostat F, which in turn is joined to the ammeter G, from which the current passes to the lamp of the Tyndallmeter through the switch H. The ammeter G is kept set at three amperes when readings are made.

The wooden horse which has been employed for the support of the Tyndallmeter is simple in construction but very convenient for adjusting the apparatus to any angle that suits the observer.

Although all readings of soil dispersoids in the Tyndallmeter are made in a dark room, it is found very trying to the eyes to determine the end-point, owing to the difficulty of matching the intensity of the lights when the colors are different. A screen placed in the eyepiece makes the readings much easier to obtain. It is prepared essentially as described by Crabtree[4] by clearing an unexposed Hammer photographic dry plate in a regular hypo solution and then thoroughly washing and drying it. The plate, gelatin side up, is put in a developing tray containing a filtered solution of 0.1 per cent of Aniline Brown and allowed to adsorb the color for 10 min. The tray should be tilted back and forth for a short time when the plate is first immersed and then at intervals, as this procedure tends to make a more uniformly colored plate. At the end of this time the plate is rinsed for 1 min. in ice cold water and dried where it will be free from dust. The plate is cut in small squares, and three thicknesses are placed in the eyepiece. A test with and without the screen showed that more uniform readings were obtained with it.

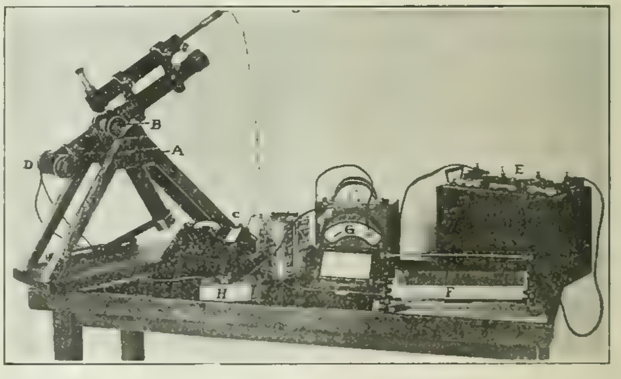


Fig. 1

Standardization

It is necessary to standardize the light of the illuminometer and that for the Tyndall beam.

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[1] Received August 3, 1921.

[2] R. C. Tolman, L. H. Reyerson, E. B. Vliet, R. H. Gerke, and A. P. Brooks, "The Relation between Intensity of Tyndall Beam and Concentration of Suspensions and Smokes," *J. Am. Chem. Soc.*, **41** (1919), 300.

[3] "A Tyndallmeter for the Examination of Disperse Systems," *J. Am. Chem. Soc.*, **41** (1919), 297.

[4] "How to Make, Fit and Use Light Filters," *Amateur Photographer and Photographic News*, **49** (1909), 173.

The illuminometer light is standardized with the apparatus made for that purpose by Leeds and Northrup Co. Since the standardization has been described by Tolman and Vliet it will not be repeated here. In our work the lamp is adjusted so that the actual number of apparent foot candles is only one-half as many as indicated by the illuminometer scale. The number of mil-amperes required to keep the lamp at this adjustment is maintained in all tests.

The light for the Tyndall beam is standardized by means of a silica suspension prepared in the following manner: One-half gram of silica, ground to pass a 200-mesh sieve, is suspended in one liter of distilled water in a 2-liter flask, and after 2 min. 300 cc. of the suspension are withdrawn by a pipet. The tip of the pipet is kept 2 cm. below the surface. Two hundred cc. of distilled water are added to the 300 cc. and the resulting dilution is employed as the standard.

The special glass tubes in which the dispersoid is examined are 12 cm. long by 4.3 cm. in outside diameter and the glass is approximately 1 mm. thick. The tubes are first filled with distilled water and closed with a 1-hole rubber stopper to prevent the inclusion of air bubbles, and are examined in the apparatus to determine whether any correction is necessary for the reflection of light from the glass. The correction is so small that it has been ignored. The silica standard is then placed in the tube and ten consecutive readings made by each of the two observers. Five readings should be made by approaching the end-point from the zero and five from the maximum end of the scale as described by Tolman and Vliet. This standard solution is kept in a well-sealed flask and employed for the frequent standardization of the apparatus.

METHODS

The soil samples are passed through a 7-mesh sieve to remove plant tissue and small stones and to produce a uniform texture, and they are then thoroughly mixed. The sifting and mixing are done as rapidly as possible to prevent loss of moisture by evaporation. The moisture content of the soil is then determined by air-drying two 25-g. quantities from each sample.

When the percentage of moisture is known, four portions are weighed out from a sample so that each one is equivalent to 5 g. of air-dry soil. These portions are placed in 1-liter Erlenmeyer flasks, and 500 cc. of distilled water are added. The flasks are stoppered and shaken vigorously for 5 min. and allowed to stand for 1 min., when 50 cc. of the suspension are withdrawn from each with a pipet by inserting the tip 2 cm. below the surface. The four 50-cc. aliquot portions are run into a 2-liter Erlenmeyer flask and diluted, if necessary, with a measured quantity of distilled water so as to give a reading between 1 and 10 on the Tyndallmeter scale. The investigator will soon find that he can readily estimate the concentration between these points. If the suspension is more disperse than desired a second 50 cc. from each flask may be added to it. The composite suspension is shaken vigorously for 1 min. and allowed to stand 24 hrs. At the end of this time all but 200 cc. of the supernatant suspension is siphoned into a flask and well shaken for 1 min. to insure uniformity. Two of the special tubes are filled with the suspension and read in the Tyndallmeter. A similarly prepared composite suspension is also read as a check on the first one.

The factor for the concentration of the disperse system is obtained by converting the actual apparent foot candle reading to the theoretical value for 1 g. of air-dry soil. The formula employed for this purpose is

$$X = \frac{vdr}{2w}$$

where X is the factor for the concentration of dispersoid per gram of air-dry soil; v is the total volume of the final suspension; d is the quotient of the initial total volume, generally 2000, by the aliquot taken for the final suspension, usually 200; r is the Tyndallmeter reading; w is the weight in grams of air-dry soil employed to make the initial total volume of suspension.

TABLE I—READINGS OF SUSPENSIONS FROM SOIL 32

	Suspension A_1		Suspension B_1	
	3.00	2.60	3.02	2.91
	2.98	2.55	3.07	2.79
	2.90	2.65	3.10	3.03
	2.90	2.80	2.90	3.13
	2.95	2.65	3.05	2.93
	2.90	2.85	2.88	2.75
	2.80	2.69	3.05	3.00
	2.85	2.90	3.00	2.80
	2.91	2.70	3.00	2.91
	2.85	2.79	2.97	3.04
Av.	2.904	2.718	3.004	2.929
	Suspension A_2		Suspension B_2	
	3.02	2.87	3.15	3.10
	3.10	2.79	3.04	2.85
	2.85	2.84	2.94	2.85
	2.85	2.91	2.95	3.05
	3.10	2.71	2.96	3.07
	2.90	3.09	3.00	2.91
	2.98	3.02	3.10	3.20
	2.88	2.78	3.11	3.02
	2.85	2.85	3.00	2.77
	2.85	2.90	2.95	2.97
Av.	2.938	2.876	3.020	2.979

DATA

The factor for the concentration of disperse phase obtained by the method outlined has been determined in thirty-one soils of different agricultural values. The first eight (6 to 13, inclusive) were kindly sent in by Dr. A. W. Sampson of the Great Basin Experiment Station, Ephraim, Utah. They are soils that have been overgrazed and are now supporting weed growth in different stages of succession. The soils numbered 31 to 34, inclusive, were collected by the junior author as representatives of types used in Massachusetts cranberry bogs. For all the remaining samples from different parts of the country our thanks are due to Dr. C. F. Marbut, in charge of Soil Survey Investigations, Bureau of Soils, U. S. Department of Agriculture.

Most of the soils gave duplicate suspensions that checked very closely, but a few, on account of their nature, gave suspensions showing greater differences. In Table I is given an example of the results that may be obtained by carefully following the procedure outlined.

TABLE II

SAMPLE No.	Soil Group	Soil Type	Source	Mean Reading	Dispersoid Concentration Factor
10	Clay and clay loam	Clay loam	Utah	1.016	191
7		Clay loam	Utah	1.685	211
12		Clay loam	Utah	1.117	356
9		Clay loam	Utah	1.031	387
11		Clay loam	Utah	1.656	621
25		Clay	Texas	2.850	712
8		Clay loam	Utah	3.063	1532
13		Clay loam	Utah	5.538	2077
30		Clay	Alabama	7.380	3690
6		Clay loam	Utah	8.230	4115
26		Clay loam	Utah	14.390	7195
24		Clay	Texas	22.840	22840
18	Silt and silt loam	Loam	Indiana	1.634	82
28		Silt loam	Idaho	1.113	223
20		Silt loam	N. Dakota	2.631	263
21		Silt loam	N. Dakota	5.558	278
37		Silt loam	Idaho	3.577	711
14		Silt loam	Kentucky	2.178	1089
17		Silt loam	Nebraska	7.519	2820
15		Silt loam	Kentucky	8.196	4057
22		Silt loam	New York	11.150	5575
27		Silt loam	N. Carolina	12.600	6300
16		Silt loam	Nebraska	14.620	7500
33	Sand and sandy loam	Sand	Massachusetts	Trace	Trace
19		Sandy loam	Indiana	1.085	51
29		Sand	Alabama	1.470	74
36		Sand	Michigan	4.730	237
35		Sandy loam	Michigan	1.316	329
31	Bogland	Sandy muck	Massachusetts	Trace	Trace
34		Bogland	Massachusetts	1.510	76
32		Woodland muck	Massachusetts	2.920	459

The average reading of Suspensions A_1 and A_2 is 2.859; of Suspensions B_1 and B_2, 2.984. The mean of these readings is 2.922, and the variation of the averages from this is 2.2 per cent.

In Table II are the results obtained from the thirty-one soils. It will be noticed that the mean readings do not increase in the same order as the dispersoid concentration factors. This difference is due to the fact that the mean readings were made with dilutions of dispersoid that varied for the different soils.

An examination of the readings obtained with these soils shows that the average error from the mean is 2.54 per cent. In obtaining this figure the results of five soils are omitted on account of abnormally high percentage errors. No effort was made to get closer checks on these samples, because four of the factors were so low and one so high that an exact check would not in any case have altered the relative values of the soils.

The relation of these dispersoid concentration factors to the other data that have been obtained will be discussed in a future report.

Summary

A procedure is given for obtaining by means of a Tyndallmeter a factor for the concentration of dispersoid in a soil.

The Determination of Glycerol in the Presence of Sugars[1]

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The accurate estimation of glycerol in transparent soaps is attended with difficulty on account of the cane sugar which is almost invariably present.

Available Methods for Glycerol Analysis

It is obvious that the sugar will oxidize, in part at least, and give rise to uncertain results if an attempt is made to determine glycerol by the Hehner method,[2] in which the sample is oxidized with potassium dichromate in acid solution. The acetin method of Benedikt and Cantor[3] is open to the objection that sugars, having numerous hydroxyl groups, are acetylated by acetic anhydride in much the same manner as glycerol.[4]

The alkaline permanganate method of Benedikt and Zsigmondy[5] should theoretically work on a mixture of glycerol and sugar, since it depends on the supposition that glycerol only is oxidized to oxalic acid by potassium permanganate in alkaline solution. As a matter of fact, however, invert sugar was subsequently found to be quantitatively oxidized to oxalic acid by this method. A test made in our laboratory showed that an amount of oxalic acid equivalent to practically 100 per cent of the theoretical quantity was produced when pure invert sugar was subjected to oxidation with alkaline permanganate in the usual way. This method as applied to straight glycerol analyses has been adversely criticized by Lewkowitsch[6] and by Allen.[7] Experiments in our laboratory have indicated that the method gives low results on crude and C. P. glycerols. The method is tedious and cumbersome, and a more convenient method capable of giving better results on glycerol was therefore sought. The isopropyl iodide method of Zeisel and Fanto[8] was not considered because it has been sharply criticized by Lewkowitsch,[9] and is moreover complicated, tedious, and of doubtful accuracy in presence of sugar.

The most usual method of determining glycerol in the presence of sugar is of course that of Donath and Mayrhofer,[10] or one of its various modifications, in which the sample is treated with lime or baryta to render the sugars insoluble, and the glycerol is extracted from the nearly dry mixture with various solvents. Any chemist who has ever tried this method cannot but have been impressed with its tediousness, many chances of losses, and resultant inaccuracy.

The method of Cook,[11] which is really an adaption of the Shukoff and Schestakoff[12] method for the determination of glycerol in meat and meat extracts, would not appear to be applicable in the presence of sugar since it is, in effect, merely an acetone extraction of the sample which has been dehydrated by mixing with sand and anhydrous sodium sulfate, and does not render sugar insoluble if present. Methods such as precipitation of glycerol with copper sulfate,[13] distillation of glycerol *in vacuo* from a solution containing sugar or salts,[14] distillation *in vacuo* with the aid of sandalwood oil[15] or precipitation as sodium glyceride[16] were examined and found inapplicable to the present problem.

Experiments with the Donath and Mayrhofer Method

An attempt was made to apply this method to the present problem, using known weights of pure sugars and glycerol of known purity. Glycerol is normally determined in a sample of soap by cracking with dilute sulfuric acid and determining glycerol in the acid filtrate by the dichromate or acetin methods. In the case of a transparent soap containing cane sugar, the acid filtrate would contain the sugar in the form of invert sugar. Hence in the experiments known equal weights of pure dextrose and pure levulose, *i. e.*, invert sugar, were used.

These results showed that continued extraction with acetone gradually dissolved the sugars. The difficulty of determining when extraction was complete and of removing all of the solvent without losing glycerol was so great and the results were so unreliable that no further work was done with the method.

Quantitative Oxidation of Sugar and Glycerol by Potassium Dichromate in Acid Solution

It seemed to the authors that it should be possible to oxidize a mixture of sugar and glycerol quantitatively with dichromate. Since the sugar in such a mixture could be readily determined by a method like that of Munson and Walker[17] it would be possible to calculate the glycerol.

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[1] Received January 26, 1921.

[2] *J. Soc. Chem. Ind.*, **17** (1898), 330.

[3] *Ibid.*, **7** (1888), 696.

[4] The acetin method was applied in our research laboratory to 0.5 g. of invert sugar. As dextrose and levulose both contain five hydroxyl groups a pentacetate might be expected to form under suitable conditions. It was found that invert sugar apparently took on 4($C_2H_3O_2$) groups, or, as is more likely, acetylated to a mixture of acetates, whose net average was a tetracetate, since the above quantity of invert sugar gave a recovery of 95.3 per cent on the assumption that tetracetates were formed.

[5] *J. Soc. Chem. Ind.*, **5** (1885), 610.

[6] "Oils, Fats and Waxes," 5th Ed., I, 447.

[7] "Commercial Organic Analysis," 4th Ed., XI, 457.

[8] *Z. landw. Versuchw.*, **5** (1902), 729.

[9] *Loc. cit.*, I, 450.

[10] *Z. anal. Chem.*, **20** (1881), 383.

[11] *J. Assoc. Official Agr. Chem.*, **1** (1915), 279.

[12] *Z. angew. Chem.*, **18** (1905), 294.

[13] *C. A.*, **6** (1912), 1072.

[14] *Ibid.*, **8** (1914), 772.

[15] *J. Am. Pharm. Assoc.*, **4** (1915), 75.

[16] *C. A.*, **11** (1917), 216.

[17] *J. Am. Chem. Soc.*, **28** (1906), 663; **29** (1907), 541; **34** (1912), 202.

Expt. I—Donath and Mayrhofer Method

Solvent: Equal parts, absolute alcohol and ethyl ether.

Conditions: Mixture of 0.125 g. dextrose, 0.125 g. levulose, 0.25 g. C. P. glycerol (96.23 per cent), and 25 cc. water, evaporated at 60° C. nearly to dryness, after addition of 0.750 g. hydrated lime, and sand. Residue extracted with successive portions of ether-alcohol, which was evaporated at low temperature, and glycerol in residue determined by dichromate method.

Recovery of Glycerol:

Test	Per cent
I	54.0
II	81.97
III	91.66

Expt. II—Donath and Mayrhofer Method

Solvent: Redistilled acetone.

Conditions: Test I—Same weight of materials as used in Expt. I; residue extracted with successive portions of solvent in the evaporating dish; glycerol determined by dichromate method. Test II—Same weight of materials as in Test I; dried residue extracted in Soxhlet extractor for 10 hrs.

Recovery of Glycerol:

Test	Per cent
I	67.4
II	164.1

Potassium dichromate should act upon invert sugar in acid solution according to the following balanced equation:

$$\underset{181.26}{C_6H_{12}O_6} + \underset{1176.8}{4\,K_2Cr_2O_7} + 16H_2SO_4 = 6\,CO_2 + 4Cr_2(SO_4)_3 + 4\,K_2SO_4 + 22\,H_2O$$

The regular Hehner or dichromate method for glycerol uses a potassium dichromate solution containing 74.552 g. per liter (1.5204 *N*), of which 1 cc. is equivalent to 0.0100 g. of glycerol. According to the above equation, 1 cc. of a 1.5204 *N* dichromate solution should be equivalent to 0.01142 g. of invert sugar.

It was found by experiment that the Hehner method applied in the usual way to a known weight of a pure hexose sugar gave a recovery of about 85 per cent. It was discovered, however, that pure dextrose and levulose were completely oxidized if a large excess of both potassium dichromate and of sulfuric acid was used. Samples of dextrose and levulose of known purity were separately oxidized; the dextrose gave a recovery of 99.90 per cent and the levulose 99.75 per cent, an average of 99.83 per cent. Hence it may justifiably be said that pure invert sugar, *i. e.*, one-half each of dextrose and levulose, which would result from the acid hydrolysis of sucrose in dilute solution, is, within the limits of experimental error, quantitatively oxidized by potassium dichromate under the proper conditions. Similarly, C. P. glycerol of known purity gave a recovery of 100.06 per cent when oxidized in a solution containing a large excess of dichromate and sulfuric acid.

Pure sucrose oxidized directly by the new dichromate method gave a recovery of 99.98 per cent, as was to be expected, since it must be inverted rapidly in the hot acid solution.

There is one transparent soap on the market which, by test, contains no sugar. Analyses for glycerol by the writers' method were made on this soap and on a sample of the same soap to which 10 per cent cane sugar was added, with the following results, expressed in per cent:

	(1)	(2)	(Av.)
Glycerol in original sugarless transparent soap.....	3.43	..	..
Glycerol in soap + 10 per cent cane sugar.........	3.34	3.40	3.37

Application of the Method to Transparent Soaps

This preliminary work proved that the method would oxidize quantitatively a mixture of invert sugar and glycerol (or of cane sugar and glycerol since cane sugar would of course rapidly become invert sugar in the strongly acid solution used). The method was accordingly applied to the analysis of transparent soaps containing glycerol.

Five samples of transparent soap were analyzed for cane sugar by the regular Munson and Walker method,[18] and for glycerol by the writers' method, with the following results. Each of the check results represents a complete separate determination.

Soap	Per cent Cane Sugar			Per Cent Glycerol		
	Sample 1	Sample 2	Av.	Sample 1	Sample 2	Av.
I	11.76	11.90	11.83	10.27	10.14	10.21
II	5.15	5.25	5.20	12.80	12.85	12.83
III	11.56	11.61	11.59	8.89	8.91	8.90
IV	...	2.72	...	18.30	18.30	18.30
V	...	17.45	...	8.13	8.13	8.13

The only precaution necessary to secure concordant results on transparent soaps was completely to remove the alcohol, which these soaps invariably contain, by boiling the acid filtrate, obtained by cracking the soap, for 20 to 30 min.; otherwise the alcohol remaining would be oxidized by the dichromate and give high and discordant results.

Other Applications of the Method

In the limited time available the authors were able to try the method on only three other types of products.

FERMENTED PRODUCTS—It is often necessary in food analysis to determine glycerol in fermented products, such as vinegar or alcoholic beverages. The authors believe that their method can be successfully used in such cases instead of the Donath and Mayrhofer method. Alcohol can be removed readily by boiling or repeated evaporation, and acetic acid appears not to be oxidized by potassium dichromate and sulfuric acid. (Blanks on the dichromate method, run with and without the addition of a known weight of sodium acetate, showed that no dichromate was consumed; hence no acetate was oxidized.) In fact, some modified dichromate methods for the determination of glycerol, such as those of Steinfels[19] and Little and Fenner[20] use lead or silver acetate in the preliminary purification of samples.

GRAPE JUICE—The difficulty would lie in the complete removal of organic matter other than sugar or glycerol by clarification. The method was tried out on unfermented Concord grape juice (containing no glycerol) both before and after the addition of a known amount of glycerol. The sample was clarified with basic lead acetate and the excess lead removed with anhydrous sodium sulfate. Analyses for sugars by the Munson and Walker method showed 14.81 per cent reducing sugars (calculated as dextrose) and 0.11 per cent cane sugar, or a total of 14.92 per cent. When total sugars were determined on this sample by dichromate oxidation, according to the authors' method, 14.85 per cent were found, a recovery of 99.5 per cent. Oxidation of the sample containing glycerol gave practically 100 per cent recovery. This shows quite conclusively that clarification was complete and that nothing oxidizable but the sugar remained in the solution. Obviously, the method could be applied to the determination of glycerol in a fermented grape juice, and it should also be applicable to the determination of glycerol in vinegar.

NONALCOHOLIC FLAVORING EXTRACTS—Recently there have come upon the market nonalcoholic flavoring extracts in which glycerol replaces alcohol. An analysis for glycerol was made by the authors' method on a vanilla extract which also contained sugar. The sample was clarified with basic lead acetate, and the excess lead removed with anhydrous sodium sulfate. Sugar determination by the Munson and Walker method showed 1.05 per cent sugars, expressed as invert sugar, and 4.25 per cent sucrose—a total of 5.52 per cent sugars, expressed as invert sugar. Glycerol as determined by the writers' method was found to be 47.42 per cent. A determination of glycerol by the acetin method on the same sample showed 49.24 per cent, a high value on account of the sugar present. The result of 47.42 per cent was stated by the manufacturer to agree very closely with his manufacturing formula.

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[18] "Methods of Analyses of the A. O. A. C.," 1920 Ed., 78.

[19] *Seifensieder-Ztg.*, **42** (1915), 721; *C. A.*, **9** (1915), 3371.

[20] *J. Am. Leather Chem. Assoc.*, **11** (1917), 254.

COMMERCIAL GLUCOSE—Attempts were made to apply the method to the analysis of a mixture of commercial glucose and glycerol. The glucose had a specific rotation of $\alpha_{D836} = 132.0°$, and contained 85.48 per cent solids. When oxidized by the authors' method it showed an equivalent hexose sugar content of 90.60 per cent and 90.63 per cent in check analyses. Repeated attempts to determine the dextrose equivalent of this glucose by the Munson and Walker method, after supposedly complete hydrolysis of the sample, invariably led to low results. Variations in the conditions of hydrolysis, *i. e.*, concentration of solution, strength of acid, kind of acid, duration of hydrolysis, and temperature, were tried without satisfactory results, the highest dextrose equivalent obtained being 85.4 per cent. Since the solids of the sample were 85.48 per cent, of which an appreciable proportion were dextrins and other intermediate products of the hydrolysis of starch, it was obvious that the dextrose equivalent of the solids must be greater than the solids themselves.

If calculated with aid of the composition-specific rotation diagram worked out by Rolfe and Defren[21] for acid-hydrolyzed starch products, the dextrose equivalent of the solids in a glucose of $\alpha_{D386} = 132°$ and total solids of 85.48 per cent will be found to be 91.3 per cent, a figure which agrees quite closely with those obtained by dichromate oxidation.

Obviously, the authors' method cannot be used to estimate glycerol in the presence of commercial glucose, on account of the fact that no satisfactory method now exists for accurately and quantitatively determining the dextrose equivalent of the solids in commercial glucose. In the unusual event that a sample of the glucose was available which was known to have been mixed with the glycerol, in which admixture it was desired to know the glycerol content, the method could be applied by finding the ratio between the dextrose equivalent of the glucose as determined by oxidation and by copper. In such a case, however, it would be far simpler and probably more accurate to determine the glucose by the polariscope. Experiments in our laboratory have shown that glycerol has no effect, positive or negative, on the optical rotation of commercial glucose.

Directions for Methods

AS APPLIED TO GLYCEROL IN TRANSPARENT SOAPS—Dissolve 25 g. of soap, accurately weighed, in 300 cc. of hot water in a 600-cc. beaker, add 50 cc. of 1 : 4 sulfuric acid, boil gently for 20 to 30 min. to volatilize any alcohol present and to invert the cane sugar completely so that it can be estimated by the Munson and Walker method. Cool the beaker, remove the cake of fatty acids, rinse the cake with distilled water, transfer the acid solution and rinsings to a 1000-cc. graduated flask, add about 0.5 g. of silver sulfate to precipitate traces of chlorides and soluble fatty acids, make up to the mark, mix the contents thoroughly, and filter. Determine the invert sugar in 50-cc. aliquot portions of the solution (equivalent to 1.25 g. of sample) by the Munson and Walker method.

For the oxidation of sugar and glycerol transfer a 50-cc. portion of the above solution to a 400-cc. beaker, using an accurately calibrated pipet or buret, add accurately with a buret or standard pipet 75 cc. of strong potassium dichromate (74.552 g. per liter, of which 1 cc. = 0.0100 g. glycerol) and then add 25 cc. 1.84 sulfuric acid. Cover immediately with a watch glass, immerse the beaker in a steam bath, and oxidize for 3 hrs. Run a blank with 100 cc. water, 25 cc. 1.84 sulfuric acid and 25 cc. strong dichromate (accurately measured with a buret or pipet), heating as described above. Make up the cooled solutions to 1000 cc. in graduated flasks, mix thoroughly and determine the excess dichromate in 50-cc. aliquot portions (one-twentieth of the oxidized solutions of blank) by adding 50 cc. of water and 20 cc. of 10 per cent potassium iodide solution and titrating the liberated iodine with 0.1*N* sodium thiosulfate.

Calculate results as in the following example:

50 cc. of oxidized solution (1/20 aliquot part) required 37.26 cc. 0.1 *N* $Na_2S_2O_3$.

50 cc. blank (1.25 cc. strong $K_2Cr_2O_7$) required 19.00 cc. 0.1 *N* $Na_2S_2O_3$.

Cane sugar (Munson and Walker method) = 11.83 per cent.

Invert sugar (cane sugar × 1.053) in 50 cc. taken for oxidation = 0.1183 × 1.053 × 1.25 = 0.1557 g.

∴ Invert sugar in 50 cc. taken for titration = 0.007785 g.

1 cc. $K_2Cr_2O_7$ (74.552 g. per 1.) = 0.01142 g. invert sugar.

∴ 0.007785 g. invert sugar required 0.682 cc. $K_2Cr_2O_7$.

Excess $K_2Cr_2O_7$ in 50-cc. portion titrated =

$$\frac{37\ 26}{19.00} \times 1.25 = 2.451 \text{ cc.}$$

$K_2Cr_2O_7$ used to oxidize glycerol in 1/20 aliquot titrated =

$$\frac{75}{20} - (0.682 + 2.451) = 0.617 \text{ cc.}$$

$$\text{Per cent glycerol} = \frac{0.617 \times 0.0100 \times 20 \times 100}{1.25} = 9.87$$

The above calculation can be readily simplified to four equations as follows:

Let a = per cent cane sugar in the sample.

b = cc. 0.1 *N* $Na_2S_2O_3$ required to titrate 1/20 aliquot portion of the oxidized portion of the sample.

c = cc. 0.1 *N* $Na_2S_2O_3$ required to titrate 1/20 aliquot portion of the blank.

A = cc. strong $K_2Cr_2O_7$ used by the sugar in 1/20 aliquot of the portion oxidized.

B = cc. strong $K_2Cr_2O_7$ in excess in 1/20 aliquot of the portion oxidized.

C = cc. strong $K_2Cr_2O_7$ required to oxidize the glycerol in 1/20 aliquot of the portion oxidized.

D = per cent glycerol in sample.

$$\text{Then } A = a \times 0.05761 \qquad (1)$$

$$B = \frac{b}{c} \times 1.25 \qquad (2)$$

$$C = 3.75 - (A + B) \qquad (3)$$

$$D = C \times 0.01 \times 20 \times 100 = 16\,C \qquad (4)$$

Special attention is called to the fact that in the calculations the values A, B, and C are carried out to 0.001 cc. This accuracy is warranted because the titrations are all made with 0.1*N* $Na_2S_2O_3$ and referred back to the strong dichromate whose normality is 1.5204.

FOR SAMPLES OTHER THAN TRANSPARENT SOAPS—Use a sample of such size that the aliquot part finally used for oxidation does not contain over 0.3 g. of sugars plus glycerol. Different samples may require different treatment to purify them from interfering substances, but the writers' results have shown that alcohol and albuminous materials can be readily removed and do not interfere.

Summary

1—The writers have evolved a modified dichromate oxidation method which will determine glycerol quantitatively in the presence of cane sugar, or of reducing sugars of such a nature that they can be quantitatively estimated by some copper reduction process.

2—The method is simple, requires no elaborate preparation of the sample, no special apparatus, and can be carried out in practically the same time as the usual glycerol analysis by the dichromate method.

3—The method has been shown to give very consistent and accurate results for the determination of glycerol in transparent soaps containing sugar, and glycerol in nonalcoholic vanilla extract containing sugar.

4—It is believed that the method can be applied also to the determination of glycerol in fermented products.

5—The method cannot, however, be applied to the determination of glycerol in the presence of commercial glucose, owing to the lack of a method which will determine accurately the dextrose equivalent of total saccharine matter in commercial glucose.

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[21] *J. Am. Chem. Soc.*, **18** (1896), 869.

The Determination of Acid Number of Tung and Other Vegetable Oils[1,2]

By L. L. Steele and G. G. Sward

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Recently Jameson[3] has shown that the heat test for the purity of tung oil (the length of time in minutes necessary to cause polymerization or jellying of the oil at an arbitrary temperature) is influenced greatly by the free fatty acid content of the oil. Gardner[4] has shown that the length of time necessary for the jellying of tung oil in the heat test is increased in direct proportion to the amount of free fatty acid of tung oil added.

As Jameson points out, the free fatty acid content of tung oil is important and he recommends that the present maximum allowable percentage of free acid be reduced to 1 per cent. (Standard specifications of the American Society for Testing Materials allow not over 3 per cent.)

It was noticed at the Bureau of Standards that different acid values were obtained upon a given sample of tung oil when alcohol and alcohol-benzene, respectively, were used as solvents. Gardner and Coleman[5] showed that the acid value of a varnish appears to be higher when alcohol-benzene mixture is used as a solvent than when alcohol alone is employed. Jameson made use of a mixture of alcohol and benzene as a solvent in the titration of the free fatty acid of tung-oil samples.

It seemed desirable to find out whether the higher acid values of tung oil in alcohol-benzene mixture were abnormal or whether the present standard use of alcohol[6] as a solvent leads to low values. In this connection it seemed desirable also to investigate the use of alcohol-benzene mixture as the solvent for other oils in the acid number determination. A third point included was the investigation of two other factors affecting the method of determining acid numbers of vegetable oils, namely, the possible influence of caustic soda, now commonly substituted for caustic potash, and the difference, if any, between the use of aqueous and alcoholic alkali in the titration of free fatty acid.

METHOD OF PROCEDURE

The acid number of a sample of commercial tung oil was determined by the standard method as follows: Four portions of 5 to 10 g. each were weighed into flasks and heated on a hot plate under a reflux condenser for 30 min. with 50 cc. of ethyl alcohol, previously made neutral to phenolphthalein. After cooling, the four samples were titrated with 0.1 *N* aqueous sodium hydroxide, 0.1 *N* alcoholic sodium hydroxide, 0.1 *N* aqueous potassium hydroxide, and 0.1 *N* alcoholic potassium hydroxide, respectively. Commercial samples of cottonseed and linseed oils were titrated in the same manner with the four standard alkali solutions.

The titrations on the oils were repeated, substituting for the alcohol 50 cc. of a neutral mixture of equal parts by volume of ethyl alcohol and C. P. benzene. In this case the oils dissolved in the alcohol-benzene mixture without heating, and titrations were made at once (omitting the half-hour heating period).

The fatty acids of each of the three oils were prepared by the usual method and each sample of fatty acid was titrated in both alcohol and alcohol-benzene as solvent, using the four standard alkali solutions. Weighed amounts of the fatty acids were added to weighed amounts of the corresponding oil, so as to form a series of oils of ascending acid numbers. These samples of oil of known acid content were titrated with both alcohol and alcohol-benzene mixture for solvent and with the four different standard alkali solutions already described.

By a comparison of the actual acid value obtained in each case with the known acid content of the oil, conclusions could be drawn as to the three points in question.

EXPERIMENTAL

OILS EXAMINED—Data were obtained upon the acid number of tung, linseed, and cottonseed oils, and of several mixtures of tung oil and rosin.

REAGENTS: *Sodium and potassium hydroxide*—C. P. sodium and potassium hydroxide sticks were used.

Alcohol and benzene—Ninety-five per cent by volume ethyl alcohol which had been recently redistilled was used. The benzene was C. P., free from thiophene. Both materials were neutralized immediately before use by titrating with alkali to a very faint pink color, using phenolphthalein as an indicator.

Standard solutions—The standard alkali solutions were prepared as for testing linseed oil,[7] except that 0.1 *N* solutions were prepared instead of 0.25 *N* solutions.

The weight of sample taken was so regulated in each case that approximately 15 cc. of the standard alkali solution were necessary for neutralization.

RESULTS OBTAINED

Table I includes values obtained upon the various oils and fatty acids.

TABLE I—ACID VALUES OF OILS AND FATTY ACIDS

	Value Found in Alcohol				Value Found in Alcohol-Benzene			
	with Aqueous		with Alcoholic		with Aqueous		with Alcoholic	
MATERIAL	KOH	NaOH	KOH	NaOH	KOH	NaOH	KOH	NaOH
Tung oil	6.60	6.76	6.52	6.32	7.05	7.15	7.22	7.15
Fatty acid of tung oil	192.7	192.4	192.6	192.4	190.3	190.1	192.9	192.1
Linseed oil	4.46	4.39	4.52	4.52	4.66	4.62	4.64	4.69
Fatty acid of linseed oil	196.9	196.6	196.0	196.8	195.9	194.9	197.1	197.2
Cottonseed oil	0.68	0.70	0.72	0.72	0.75	0.74	0.71	0.76
Fatty acid of cottonseed oil	184.1	184.7	183.1	184.2	182.1	182.7	183.6	184.4
W. W. rosin	161.8	162.1	160.7	160.1	161.2	161.4	161.2	160.6

The determinations of the acid numbers of the fatty acids of tung, linseed, and cottonseed oils were in good agreement, except in the case where aqueous alkali was used for titration with alcohol-benzene as solvent. It is probable that here there was enough dilution by the water of the alkali solution to cause some hydrolysis, giving slightly low values for the acid numbers. For this reason the two low values in the case of each sample of fatty acid were omitted and the average of the six other values was taken as the true acid number of the sample.

The acid numbers of a series of mixtures of the different oils with their fatty acids were calculated from the weights of oil and fatty acid mixed and the average acid value of the oil and its fatty acid, respectively. In the case of tung oil the average acid value found in alcohol-benzene was assumed to be the true acid number.

SUMMARY

1—The use of alcohol alone as a solvent in the determination of the acid number of tung oil leads to low values,

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[1] Received August 9, 1921.

[2] Published by permission of the Director, Bureau of Standards.

[3] *Analyst*, **46** (1920), 328.

[4] *Paint Mfrs.' Assoc. U. S., Circ.* **119**.

[5] *Paint Mfrs.' Assoc. U. S., Circ.* **87**.

[6] *Am. Soc. Testing Materials Standards*, **1918**, 577.

[7] "Recommended Specifications for Linseed Oil," Bureau of Standards, *Circ.* **82**.

especially in the case of oils with a low acid content. Alcohol-benzene mixture gives values which are correct within the limits of experimental accuracy of the determination. With rosin-tung oil mixtures, alcohol-benzene gives results nearer the theoretical than does alcohol alone.

2—Alcohol as a solvent in the determination of the acid number of linseed and cottonseed oils yields values which average slightly lower than the theoretical acid content. In most of the determinations the average of the values obtained with alcohol-benzene mixture were closer to the theoretical acid content than when alcohol was used as solvent.

3—Alcohol-benzene mixture is preferable to alcohol as a solvent because the end-point in the titration is much sharper.

4—As was to be expected, no difference was noted in any case between the use of sodium and potassium hydroxide, within the limits of experimental accuracy of the titrations.

5—If the weight of sample is so regulated that approximately 15 cc. of alkali solution are required for neutralization, aqueous alkali can be used interchangeably with alcoholic alkali, with no appreciable difference in results within the limits of experimental accuracy.

6—In the case of a material with a very high acid number (above 100), such as a fatty acid, there is evidence of some hydrolysis when aqueous alkali is used with alcohol-benzene as a solvent, and alcoholic alkali should be used for titration.

TABLE II—ACID VALUES OF MIXTURES OF OIL AND FATTY ACID

Sample No.	Calculated Acid No.	Value Found in Alcohol				Value Found in Alcohol Benzene			
		with Aqueous		with Alcoholic		with Aqueous		with Alcoholic	
		KOH	NaOH	KOH	NaOH	KOH	NaOH	KOH	NaOH
		TUNG-OIL MIXTURES							
1	15.33	14.40	14.37	14.72	14.20	15.22	15.33	15.38	15.41
2	29.25	28.3	28.3	28.7	28.6	29.3	29.1	29.4	29.3
3	59.1	58.8	58.5	58.9	58.3	59.2	59.2	59.3	59.2
4	99.3	99.2	98.9	99.0	98.7	99.3	98.7	99.4	99.2
		LINSEED-OIL MIXTURES							
1	10.61	10.45	10.41	10.55	10.42	10.54	10.52	10.51	10.60
2	24.22	23.76	24.01	24.10	23.85	24.13	24.25	24.32	24.20
3	53.2	52.86	52.88	52.97	52.85	53.15	53.13	53.05	53.18
4	100.4	100.2	99.6	99.9	100.0	100.6	100.2	100.6	100.5
		COTTONSEED-OIL MIXTURES							
1	11.29	11.07	11.05	11.25	11.22	11.39	11.33	11.65	11.34
2	25.4	25.07	24.79	25.00	25.03	25.40	25.32	25.21	25.26
3	50.7	50.4	50.5	50.4	50.6	50.6	50.6	50.8	50.8
4	101.5	101.7	101.4	100.9	101.6	100.7	101.3	100.6	101.4
		TUNG OIL-ROSIN MIXTURES							
1	15.93	15.36	14.81	15.33	15.53	15.75	15.87	15.75	15.98
2	29.7	28.42	28.33	28.25	28.75	29.32	29.13	29.25	29.50
3	60.7	60.2	59.8	59.7	60.3	60.4	60.3	60.4	60.6
4	102.8	102.0	102.2	102.0	103.0	101.8	102.2	102.8	103.2

Vapor Pressure Determinations on Naphthalene, Anthracene, Phenanthrene, and Anthraquinone between Their Melting and Boiling Points[1,2]

By **O. A. Nelson** and **C. E. Senseman**

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A search of the literature on vapor pressures reveals the fact that very few determinations have been made on most of the solid hydrocarbons between the temperatures of their melting and boiling points, or above. In view of this fact and also in response to the increased demand for more reliable physical constants, arising from recent researches into different types of reactions both in the liquid and vapor phase, the problem of determining the vapor pressures of some of the more common compounds was undertaken.

In this paper the method employed will be discussed, and some of the results obtained in naphthalene, anthracene, phenanthrene, and anthraquinone will be tabulated. In subsequent publications the results on other compounds, or mixtures of compounds, which are now under investigation will be given.

Up to the present time vapor pressure determinations of compounds of the type in which we are interested seem to have been limited to comparatively low temperatures. Ramsey and Young[3] determined the vapor pressures of camphor between 0° and 180° C.; Vanstone,[4] that of a mixture of camphor and borneol between 78° and 185° C., while Allen[5] worked with naphthalene between 0° and 130° C. Perman and Davis[6] determined the vapor pressure of naphthalene, and of mixtures of naphthalene and β-naphthol at 70° C., and Barker[7] determined the pressures of naphthalene at 20°, 30°, and 40° C. From the vapor pressure curves obtained by Stelzner,[8] it appears that this investigator determined the vapor pressure of naphthalene between 75° and 170° and extrapolated the curve to 218° (b. p.) while in the case of anthracene observations were made for every 10° between 160° and 260° C., and on anthraquinone between 224° and 320°. It appears, therefore, that in no case did the temperatures of the experiments even approximate the boiling point of the compounds or mixtures under investigation.

METHODS OF MAKING VAPOR PRESSURE DETERMINATIONS

The static method of vapor pressure measurement and the dynamic, or air current method, have been used with different modifications so long and with so much success as to become almost standard. Other methods have been proposed, such as the optical method devised by C. and M. Cuthbertson,[9] based on the assumption that the refractivity of a vapor was proportional to the vapor pressure; or the hygrometric method devised by Forbes.[10]

The dynamic method is most suitable for low pressures and low temperature work, and has been used with varying degrees of success by Regnault,[11] Linbarger,[12] Perman,[13] Derby, Daniels and Gutsche,[14] and others. The method consists essentially in passing a known volume of air or indifferent gas over the substance whose vapor pressure is to be determined, and by determining the amount of substance carried over, the vapor pressure is readily calculated from Dalton's law of partial pressures. The air drawn through the apparatus must necessarily be saturated with the vapors, and herein lies one of the chief difficulties. The temperature of the saturator must be kept very constant for considerable periods in cases where the substance under investigation has a low vapor pressure, and this alone is not easy to accomplish especially if the required temperature is comparatively high. Even if constant vapor baths are used, a change of 5 or 10 mm. in the atmospheric pressure

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[1] Presented before the Division of Dye Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Contribution No. 53 from the Color Investigation Laboratory, Bureau of Chemistry, Washington, D. C.

[3] *Phil. Trans.*, **1884**, I, 34.

[4] *J. Chem. Soc.*, **97** (1910), 429.

[5] *Ibid.*, **77** (1900), 412.

[6] *Ibid.*, **91** (1907), 1114.

[7] *Z. physik. Chem.*, **71** (1910), 235.

[8] Dissertation, Erlanger, **1901**, "Über den Dampfdruck fester Körper" (original article not available).

[9] *Proc. Roy. Soc. London, A*, **85** (1911), 305.

[10] *Chem. News*, **106** (1912), 88.

[11] *Ann. chim. phys.*, [3] **15** (1845), 129.

[12] *J. Am. Chem. Soc.*, **17** (1895), 615.

[13] *Proc. Roy. Soc. London*, **72** (1903), 72.

[14] *J. Am. Chem. Soc.*, **36** (1914), 793.

is sufficient to cause an appreciable change in the boiling point of the liquid, and hence in the temperature of the vapor baths.

The old static method offers some advantage over the dynamic, but is by no means without objectionable features. Here again the question of maintaining at a constant temperature a long mercury-filled tube (750 mm. or more) presents itself, and also that of expelling the last traces of air or other impurities that may be dissolved in the mercury or absorbed on the inner surface of the glass tubing. For a more detailed and critical discussion of the merits and demerits of the dynamic and static methods of vapor pressure determination, the reader is referred to the work of Smith and Menzies.[15] The other methods mentioned above, as well as the dew-point and tensimetric methods, have rather limited applicability and need not be discussed in this connection.

Apparatus

The apparatus used throughout this work was a submerged-bulblet, vapor pressure apparatus, as developed by Smith and Menzies. This method seemed to offer a number of advantages not found in any of the others: the temperature could easily be controlled and the pressure could be read off directly on the manometer, thus eliminating errors due to temperature variations, insufficient stirring of the thermostat, or in condensing or absorbing and analyzing vapors, as in the air current methods. The method is also comparatively rapid, since a series of determinations may be completed in one day. The apparatus is shown diagrammatically in Fig. 1.

Instead of using an open-end pressure gage, a manometer a trifle over 1 meter in length was made from Pyrex glass tubing of 8 mm. inside diameter. The mercury used in the manometer was carefully purified by shaking with nitric acid and further by distilling three times under vacuum. Before the manometer tube was sealed off, it was very thoroughly cleaned with hot chromic acid cleaning solution, rinsed with distilled water, and dried by heating while a current of dry air was drawing through. After being filled with the mercury the manometer was carefully boiled out in order to expel all foreign materials which might be dissolved in the mercury or absorbed on the inner surface of the glass. The boiling out process lasted over 2 hrs., under pressure of approximately 3 mm. Not the slightest indication of air bubbles could be detected anywhere along the tube.

The difference in levels of the mercury in the manometer arms was measured by means of a meter stick graduated in millimeters. The accuracy of the calibrations was checked against a standard steel tape, and found to differ by about 0.5 mm. in 1000. The temperature of the manometer was observed and the readings were corrected accordingly, taking the value of the cubical coefficient of expansion of mercury given in the Smithsonian tables (0.0001818). The manometer readings were made with the naked eye and were correct to ± 0.2 mm.

The apparatus, not including the heating device and thermostat, was fastened to a board 24 in. × 13 in. and consisted essentially of three parts: manometer, A; glass connections all in one piece, and isoteniscope, H. The bottle, G, was evacuated to about 2 mm. before each run was made and was used for lowering the pressure in the system by opening stopcock E. A pressure bottle (not shown) was used for raising the pressure in the apparatus by opening the 3-way cock, D, which was also connected with the atmosphere. In cases of pressures below atmospheric the pressure bottle was not used, but D was turned so as to admit air directly from the atmosphere. A small hand pump was used to produce the necessary pressure in the bottle or in the apparatus.

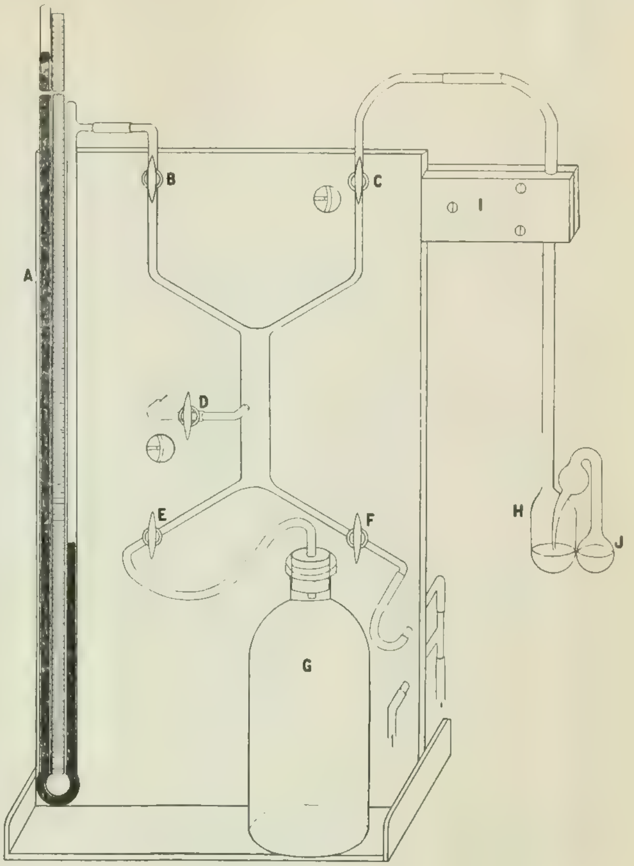

Fig. 1

The isoteniscope, or rather "dynamic isoteniscope,"[16] was made of heavy Pyrex glass and was about 45 cm. in length. The bulb containing the confining liquid[17] was 50 mm. long and 30 mm. in diameter. The side bulb containing the substance was also made of Pyrex glass, but with much thinner walls, and had a diameter of about 20 mm. This part of the apparatus could readily be detached from the rest by removing clamp I which held it in position; and since it was connected to the main part of the apparatus by a piece of rubber tubing it could easily be removed for refilling. All rubber connections were short and held a high vacuum for considerable periods. To test the different connections, as well as the stopcocks, the apparatus was evacuated to about 2 or 3 mm. and left until the following day, when an increase to only about 10 mm. was observed.

The thermostat and method for observation of equal pressure in the side bulb containing the substance under investigation and the manometer are shown in Fig. 2. A beaker of one and one-third liters capacity was used to hold the liquid bath (glycerol for naphthalene and the eutectic mixture of sodium and potassium nitrates for the higher boiling compounds) and was heated by means of an electric heater. This heater was made by winding No. 22 asbestos-covered nichrome wire on a glass beaker with a diameter a trifle larger than the one to be used throughout the observations. This wire was covered with a layer of alundum cement and dried in an electric oven. When perfectly dry it was placed in a cubical wooden box 9.5 in. on a side and insulated with packed asbestos shreds. With this amount of insulation it became an easy matter to maintain constant temperature of the liquid bath long enough to bring the pressures to equilibrium. By means of a 2-way switch, connections were made with both 110- and 220-volt circuits, the latter being used to boost the temperature to save time.

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[15] *J. Am. Chem. Soc.*, **32** (1910), 32.

[16] Smith and Menzies, *Loc. cit.*, 1448.

[17] In each determination the material constituting the confining liquid was the same as that the vapor pressure of which was being measured.

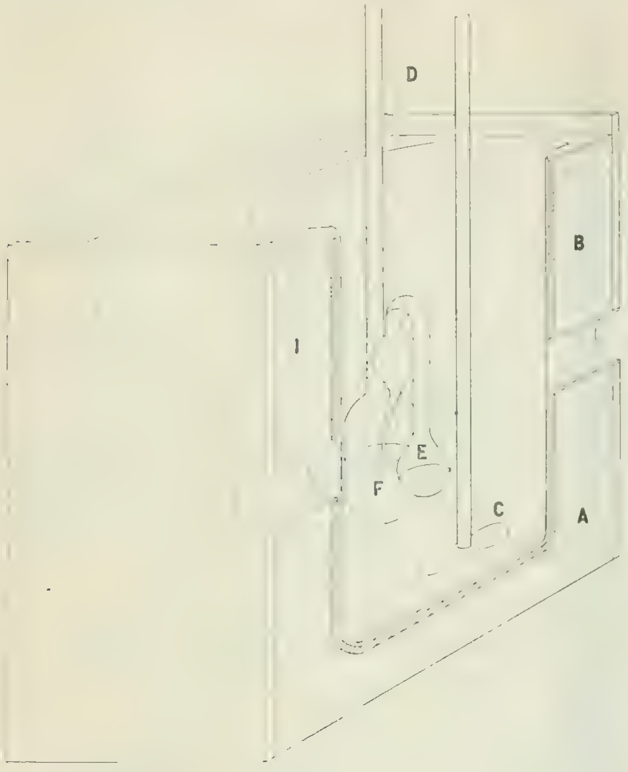

FIG. 2

A—ELECTRIC HEATER
B—PYREX BEAKER (1, 3 L.)
C—STIRRER
D—ISOTENISCOPE
E—SAMPLE BULB
F—CONFINING-LIQUID BULB
I—INSULATION: ASBESTOS SHREDS

In order to enable the worker to observe when the levels of the liquid in the tube leading from the side bulb of the isoteniscope and that of the confining liquid were the same, two holes about 1 in. in diameter were made, directly opposite, through the sides of the electric heater and the surrounding insulation. By adjusting the position of the isoteniscope in such a way that the bulb containing the confining liquid was directly in line with these holes, and by placing an electric light at the opening of one of them, observations could very easily be made through the other.

The bath liquid was kept in violent motion by a stirrer revolving at high speed.

TEMPERATURE MEASUREMENT

It is well known that for temperatures between 250° and 350° or 375° ordinary mercury thermometers cannot be relied upon. From calibrations made by the Bureau of Standards one often observes a correction of from ±1° to ±2° over a range of 50° C. Such errors are not often of much consequence in ordinary work, but in work similar to this an error of 0.1° C., near the boiling point of naphthalene, for example, would produce an error of 1.7 mm. in the vapor pressure.

Smith and Menzies used a platinum resistance thermometer, and were able to observe temperature variations of from 0.1 to 0.01° C. Inasmuch as such an instrument was not available for the present investigation, a multiple junction copper-constantan thermoelement was made, and the temperature calculated from the e. m. f. developed. From the work of Adams of the Geophysical Laboratory[18] this method of temperature measurement is shown to be perhaps the most reliable, as well as the most accurate, so far developed. Adams observed that with a single copper-constantan couple a temperature variation of approximately 0.02° C. would cause a change of 1 microvolt in the e. m. f. produced, or with a sensitive potentiometer a temperature change of 0.01° could readily be observed. Not having available a galvanometer sensitive enough to register such minute changes in e. m. f., instead of using a single couple, the writers employed a multiple element, consisting of five couples connected in series. The e. m. f. with such an arrangement, using 0° for the cold junction temperature, varied from 0 microvolts at 0° to about 94,000 microvolts at about 380°, or a change in e. m. f. of nearly 250 microvolts for a change of temperature of 1° C. The constant boiling liquids used in calibrating the thermoelement were water for 100° C., naphthalene for 217.95°, and benzophenone for 305.9°. Corrections in the boiling points of these compounds were made for changes in atmospheric pressures. To make certain that our calibrations were correct the results obtained in our laboratory at the temperature of the boiling points of water and naphthalene were checked against observations made on our thermocouple at the Geophysical Laboratory, under the supervision of Mr. Adams.

PURIFICATION OF MATERIALS

The naphthalene was obtained pure from the stock rooms and showed a boiling point of 217.95° at 760 mm. The anthracene was obtained from the commercial product (about 85 per cent) by repeated sublimations and two crystallizations from solvent naphtha, two from benzene, and one from 95 per cent alcohol. The carbazol was removed by fusing with sodium hydroxide and potassium hydroxide before the first sublimation. The final product showed a beautiful purplish fluorescence and had the same melting point as the Kahlbaum product used in one of the runs. Phenanthrene was purified in the same way as the anthracene, and had a melting point of 100° C. The anthraquinone was crystallized twice from benzene and dried for 5 hrs. at 120° C. before using.

TABLE I—NAPHTHALENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
		181.20	310.6
87.47	11.9	185.34	347.6
95.00[1]	15.5	188.30	376.5
100.00	18.5	196.96	464.1
104.39	22.9	198.53	482.1
109.65	28.7	200.50	505.7
114.70	35.9	205.78	576.2
117.15	38.3	206.00	581.9
128.06	58.7	212.17	667.8
133.72	71.2	213.30	682.7
144 45	103.5	217.34	755.8
158.95	165.1	217.87	759.2
163.13	187.1	221.45	825.2
175.10	260.8		
178.44	290.0		

[1] Allen, *Loc. cit.*, 412.

TABLE II—ANTHRACENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
226.53	52.7	297.38	317.7
227.77	52.7	298.22	319.1
231.94	60.2	304.35	363.9
232.12	62.1	310.31	415.6
236.64	69.6	318.20	488.1
244.59	86.5	321.29	515.0
254.86	113.4	325.47	555.5
259.50	129.5	329.47	612.2
261.76	135.5	335.52	674.4
263.74	142.5	337.14	692.7
270.70	169.3	337.70	697.6
271.75	175.0	340.58	738.9
277.50	203.2	341.57	756.4
277.66	198.2	341.70	757.3
286.66	247.7	342.05	761.2
292.15	279.0	343.25	778.2
295.37	303.0		

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[18] *Am. Inst. Mining Met. Eng., Bulletin* **153** (1919)

TABLE III—PHENANTHRENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
232.34	62.2	300 91	350.9
233.54	65.4	309 44	420.3
246.59	94.5	308.64	4414.8
249.14	101.5	312 62	446.0
264 73	151.4	319.27	510.7
269.89	172.4	321.24	531.5
281.33	226.1	332.11	654.4
282.73	234.1	333 08	664.6
294.57	307.4	339 91	754.3
295.37	311.4	340.41	762.3
299.88	340.2	340.59	764.2

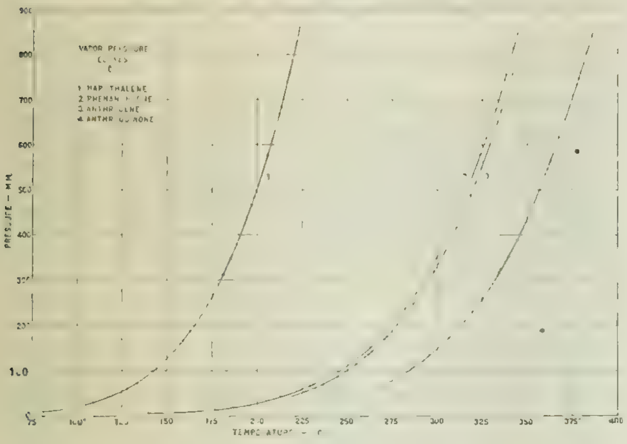

FIG. 3

TABLE IV—ANTHRAQUINONE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
285.58	104.0	346.11	402.0
286.71	108.0	349.03	428.0
292.74	122.2	351 14	448.2
295.30	133.5	357.00	500.0
302.80	156.0	361 18	546.6
306.74	172.6	362.82	562.3
311.43	189.8	364 54	579 2
315.38	209.5	367.33	615.8
319.83	230.6	370.66	656.0
321.70	241.5	373.71	685.4
325.01	259.4	377.53	733.1
329.22	282.7	378.71	746.4
330.96	296.4	379.73	759.0
334.34	317.5	381.21	779.4
335.35	323.4	382.14	791.6
339.80	352.6	383.18	804.7
344.30	388.0		

TABLE V—NAPHTHALENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
85	9.9	155	144.4
90	12.0	160	168.4
95	14.9	165	195.5
100	18.5	170	226.1
105	23.0	175	260.6
110	28.5	180	299.1
115	35.0	185	342.3
120	42.7	190	390.2
125	51.8	195	443.3
130	62.4	200	502.1
135	74.6	205	566.6
140	88.7	210	637.2
145	104.8	215	714.2
150	123.3	218	760.0
		220	797.9

TABLE VI—ANTHRACENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
220	42.6	290	265.9
225	49.5	295	297.5
230	57.3	300	332.0
235	66.1	305	269.5
240	76.0	310	410.5
245	87.1	315	454.9
250	99.6	320	502.9
255	113.5	325	554.7
260	129.1	330	610.4
265	146.5	335	669.8
270	165.8	340	732.9
275	187.3	342	760.0
280	211.0	345	799.5
285	237.2		

TABLE VII—PHENANTHRENE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
230	58.3	290	276.1
235	68.1	295	308.3
240	79.0	300	343.7
245	91.1	305	382.1
250	104.4	310	424.0
255	119.2	315	469.5
260	135.5	320	518.8
265	153.7	325	572.0
270	173.6	330	629.4
275	195.7	335	691.1
280	220.0	340	757.0
285	246.7		

TABLE VIII—ANTHRAQUINONE

Temperature ° C.	Vapor Pressure Mm.	Temperature ° C.	Vapor Pressure Mm.
285	103.0	340	354.5
290	116.2	345	392.9
295	131.3	350	435.5
300	147.8	355	481.9
305	166.0	360	531.7
310	186.0	365	585 4
315	207.9	370	643.4
320	232.0	375	703.0
325	258.5	379.8	760
330	287.5	380	763.4
335	319.4		

RESULTS OBTAINED

The results obtained in the vapor pressure determination on naphthalene, anthracene, phenanthrene, and anthraquinone are given in Tables I, II, III, and IV, respectively. Fig. 3 shows the vapor pressure curves of these compounds using the above values.

The above observations were plotted on 80 cm. × 100 cm. coördinate paper, and the pressures for intervals of 5° were read from these curves. These observations are tabulated in Tables V to VIII, inclusive, and are intended to show the mean values of all our observations on the compounds worked on thus far.

It should be pointed out that since it is hardly possible to read a manometer closer than to within ±0.1 or 0.2 mm. without the aid of a cathetometer or a vernier arrangement, the per cent error is necessarily much greater where the pressures are low; while at higher pressures the large variation due to small changes in temperatures makes observations difficult at these points. It was, however, much easier to obtain good checks at the higher pressures than at the lower, for, as pointed out in the first part of this paper, the temperature was controlled without much difficulty.

As may be seen from the above tables and curves, the boiling points of these compounds are as follows: Naphthalene 217.95° (taken from literature and used in calibrating thermocouple), anthracene 342°, phenanthrene 340.2°, and anthraquinone 379.8°. The results obtained on phenanthrene and anthraquinone agree very well with those given in the literature, namely, 340° and 380° C., respectively. For the boiling point of anthracene the literature gives 350° and 351° C.[19] but in no case was this temperature reached before the pressure reached points much above 760 mm. Further to verify the observations on anthracene at this temperature, the writers made three sets of duplicate determinations on three different samples of anthracene: two, on a sample prepared by Dr. K. P. Monroe, formerly of the Bureau of Chemistry, two, on the product purified from commercial anthracene as outlined above, and two, from a sample of Kahlbaum's. A large number of observations were made on each of these samples at about the boiling point, with an agreement well within the limits of experimental error.[20] Boiling point determinations were also made according to the method described by Mulliken, using an Anschutz thermometer, with results that again agreed with those given above, as obtained by vapor pressure determinations.

[19] Landolt-Börnstein, "Physikalisch-chemische Tabellen;" Mulliken, "Identification of Pure Organic Compounds."

[20] The experimental error referred to here is the error introduced in reading the manometer, as pointed out above, and a slight error due to inability to observe variations in e. m. f. to less than 2 microvolts corresponding to approximately 0.008° C. It should be noted, however, that the change in pressure corresponding to a change of 0.008° C. in the temperature at about the boiling point of anthracene is of the order of 0.10 mm. so the error in temperature reading becomes negligible.

SUMMARY

A brief resumé of previous vapor pressure determinations has been made.

A detailed description has been given of the method employed in obtaining vapor pressure values for naphthalene, anthracene, phenanthrene, and anthraquinone, and tables and curves of observed vapor pressures of these compounds have been recorded.

Boiling point determinations have been made on anthracene, phenanthrene, and anthraquinone with the following results: Anthracene, 342° C.; phenanthrene, 340.2° C.; anthraquinone, 379.8° C.

Experiments with Heat Interchangers[1]

By F. Russell Bichowsky

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

In liquid air machines and other refrigerators which depend on the Joule-Thomson effect for cooling, the efficiency depends, for a given intake pressure, temperature, and rate of flow of the gas, on the character of the heat insulation, and especially on the efficiency of the heat interchange between the comparatively hot incoming and comparatively cold outgoing gas. In a perfect heat interchanger, the gas entering the interchanger and the gas leaving the interchanger will have the same temperature. Assuming the intake temperature of the gas (in this case O_2) to be 298° A., and the intake pressure to be 200 atm., and assuming perfect heat interchange and perfect heat insulation, and taking for the value of the Joule-Thomson effect under these conditions $-50°$, for the molal heat capacity of the gas at 1 atm. 6.7, and for the heat of vaporization per mole 1600 cal., it can be shown that 11 per cent of the gas will be liquefied.[2] If the outgoing gas leaves the interchanger at temperatures less than that of the incoming gas, a similar calculation will show that the yield of liquid O_2 (and the same values hold approximately for liquid air and liquid N_2) will be decreased 20 per cent for each 10° difference of temperature between outgoing and incoming gas. Ordinarily, even for the comparatively poorly insulated, small-size liquefiers found in many laboratories, the loss of efficiency due to poor thermal insulation is small, compared with that due to poor interchange.

The heat interchanger commonly used on liquid air machines consists of a coil of one or more copper tubes either wound one tube inside the other, as in the original Linde design, or, as is more common in laboratory interchangers, of the Hampton type, in the form of flat coils, the first coil being wound from the center out and the next from the outside in, either one tube being used or several tubes wound in parallel. In the Linde design the compressed gas, after expansion at the lower end of the coil, passes back the entire length of the coil through the annular space between the inner and outer tubes. In the Hampton type, the gas, after expansion, passes back over the tightly wound coil through the interstices between layers left during winding. One-eighth inch o. d. drawn soft copper tubing is about as small as is practical to use, and one-fourth inch o. d. copper tubing is a convenient size.

To study the efficiency of heat interchange in such small tubes between the walls and the rapidly moving high pressure gas, the apparatus shown in Fig. 1 was constructed. The wire AC was of tested No. 40 constantan which was carefully stretched so as to be exactly central in the tube. The small leads were No. 40 copper, the whole forming a differential thermoelement giving the difference of temperature of the gas between A, B, and C. The initial temperature was given by a thermoelement not shown. The mean inside diameter of the tube was 0.124 in. (0.315 cm.), the outside 0.251 in. (0.638 cm.). The length between junctions A-B and B-C was 1.0 ft. (30.5 cm.). Table I gives typical results of many tests. In this table, temperatures are given in degrees Centigrade absolute, pressures in atmospheres, rate of flow in cu. m. per min. free gas. The figures in parenthesis in Columns 4 and 7 are corresponding values in cu. ft. per min. and °F. per ft. per deg.

TABLE I

Intake Temp. °A.	Temp. of Bath °A.	Pressure Atm.	Rate of Flow Cu. M./Min.	Temp. A-C	Diff. A-B	Temp. Modulus Deg./M./Deg.
290	90	200	0.93(33)	33	17	0.26(0.085)
240	90	200	0.93(33)	25	11	0.24(0.073)
290	240	200	0.93(33)	8	4	0.26(0.08)
240	90	100	0.93(33)	24	12	0.26(0.08)
290	240	100	0.93(33)	8	4	0.26(0.08)
290	90	200	0.47(16.5)	68	35	0.55(0.17)
240	90	200	0.47(16.5)	42	20	0.42(0.13)
290	240	200	0.47(16.5)	15	8	0.52(0.16)

The first six columns are self-explanatory; the last column gives the temperature modulus, *i. e.*, the fall of temperature per meter of tube per Centigrade degree difference of temperature between the temperature of the bath and the temperature of the incoming gas, found by dividing the values in Column 6 by the temperature head, *i. e.*, by the temperature of the bath minus the intake temperature. These results, which are only approximate, show that the temperature drop per meter of tube is independent of the pressure, inversely proportional to the rate of flow, and proportional to the temperature head from bath to incoming gas.

Knowing the modulus as defined above for a given sized tubing and given rate of flow, it is possible to calculate the length of that tubing which will be necessary to construct an ideal interchanger of given thermal efficiency.

Let T_1 = temperature of incoming gas
T_2 = temperature of gas just before expansion
T_3 = temperature after expansion (for liquid air machines this will be temperature of liquid air)
T_4 = temperature of gas leaving exchanger
C_{p_i} = molal heat capacity of incoming gas, under pressure P_i at any point along interchanger
C_{p_o} = molal heat capacity of outgoing gas, under pressure P_o at same point along interchanger
t_i and t_o = temperatures of incoming and outgoing gas at same point
M_i = mass of gas, in moles, entering interchanger in any interval of time
M_o = mass of gas leaving interchanger in same interval

Then for a liquid air machine $M_i - M_o = A$, the mass of air liquefied in that interval; or, choosing the interval so that $M_i = 1$, and assuming that the liquefier has been running long enough so that conditions do not change with the time, $1 - M_o$ equals the efficiency of the liquid air machine. Now C_{p_i} and C_{p_o} will in general be functions of the temperature, *i. e.*, $C_{p_i} = f_{p_i}(T)$ and $C_{p_o} = f_{p_o}(T)$. The function will depend on kind of gas and pressure. This may be determined by experiment.

Let l be the length of the interchanger, and let μ be the temperature modulus as defined above, *i. e.*, the drop of temperature per unit length per degree temperature head. Now the heat transferred from the incoming to outgoing gas for any small segment of the interchanger is

$$(t_i - t_o)\mu dl$$

where dl is length of segment. This equals $MC_{p_o}\,dt$ and $+\,C_{p_i}\,dt$, where dt is change of temperature of the gas in length dl. Integrating gives:

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[1] Received March 7, 1921.

[2] This is based on the equation O_2 (g. 298-50° A.) = xO_2(1, 90° A.) + $(1-x)O_2$ (g. 298° A.); $\Delta H = O$. Here x is per cent of gas liquefied and H is heat content. Details will be given by Lewis and Randall, "Treatise on Thermodynamics."

$$1 = \frac{M_O}{\mu}\int_{T_3}^{T_4} \frac{C{p_O}dt_o}{t_i - t_o} = \frac{1}{\mu}\int_{T_1}^{T_2} \frac{C{p_i}dt_i}{t_i - t_o} \tag{1}$$

$$\text{and } H = \int_{T_2}^{T_1} C{p_i}dt_i = M_O \int_{T_3}^{T_4} C{p_O}dt_i \tag{2}$$

If for any gas Cp is known as a function of T and P, these equations can be solved by usual methods. For a first approximation the value of Cp at the geometrical mean temperature may be assumed. Treating Cp as constant, and integrating, the equation becomes

$$1 = \frac{M_O C{p_O} 2.3}{\mu\left(\frac{M_O C{p_O}}{C{p_i}} - 1\right)}\left[\log(T_1 - T_4) - \log\left(\left(\frac{M_O C{p_O}}{C{p_i}}\right)(T_3 - T_4) + T_1 - T_3\right)\right] \tag{3}$$

For the present case $\mu = 0.26$, $C{p_O}$ for air at one atmosphere and 160° K. (the mean temperature of the outgoing gas) equals 7.1; for air at 200 atm. (the most convenient pressure) and 240° K. (the mean temperature of the incoming gas) $C{p_i} = 8.5$.[3] Assuming 60 per cent theoretical yield of liquid air, *i. e.*, liquid air efficiency of 7 per cent, M = 93 and $T_1 - T_4 = 50 \times 0.40 = 20°$ C. Using these values, 1 = 180 m. (550 ft.). If 80 per cent theoretical yield is assumed, 1 = 250 m. (770 ft.).

These figures accord with our experience with interchangers of the best design. Ordinarily the interchange from the low pressure return air to the tubes is by no means as efficient as that assumed here, and it is therefore not safe, unless special precautions are taken, to reduce the length of an interchanger of 7 per cent capacity to less than, say, 250 meters.

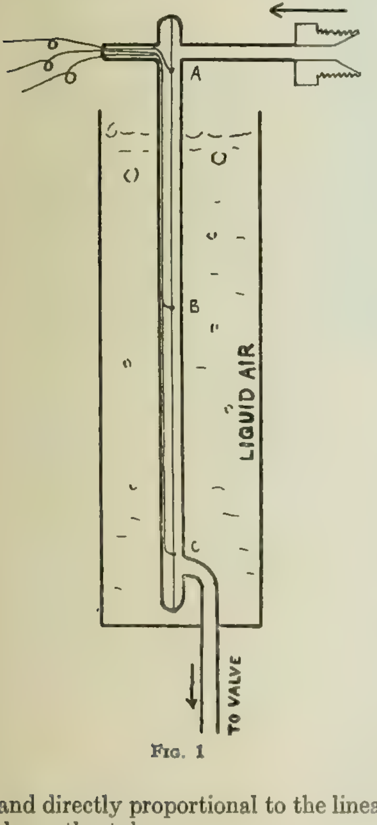

FIG. 1

It was not convenient to repeat the experiments above for different sizes of tubes, since the results for larger tubing would have no practical value to us (larger size tubing being unduly difficult to coil), and since it is doubtful that our type of apparatus would give results of much value for smaller sizes of tubing. It is thought, however, that for a given flow in free feet per minute the rate of interchange would be independent of the diameter, at least for sizes of tubing not too greatly different from one-eighth in. i. d. This approximation is based on the assumption that for constant mass velocity the rate of interchange is proportional to circumference, inversely proportional to diameter, and directly proportional to the linear velocity of gas flowing down the tube.

The problem of heat interchange between the low pressure cold gas and the copper tubing carrying the high pressure gas is not so well adapted to simple experimental investigation as the problem of heat interchange between the copper tubing and the compressed gas. In the last case the flow of gas is approximately of stream type. In the first case we have conditions which vary from nearly stream flow in the Linde type interchanger to extremely turbulent flow in the Hampton type. It is obvious that if the flow is turbulent enough so that the temperature at every point in any cross section normal to the axis of flow is the same, no matter what is the shape or length of the coil of the interchanger, provided its heat conductivity longitudinally is negligible, the same length of tubing will give the same efficiency. This makes the problem of effective interchange of heat from tube to outflowing gas entirely a problem of care in construction, particularly care in preventing the formation of stream channels causing local differences of temperature in a given cross section, and in so winding the coils that the outflowing air always has a resultant of velocity opposite to the velocity of the compressed gas.

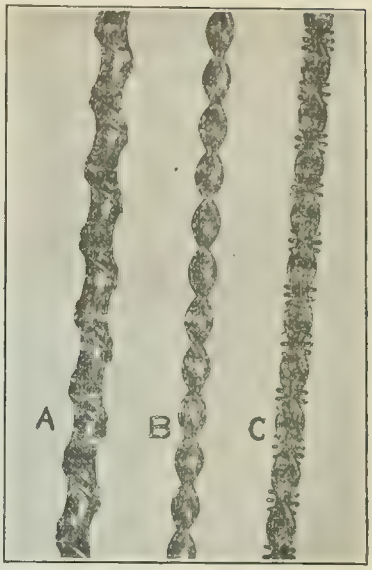

FIG. 2

The necessity for effective heat insulation of the whole interchanger is obvious, but means of providing it are familiar and need not be discussed.

THE NELSON INTERCHANGER

The chief objections to the type of interchanger described above are the length of copper tubing required, making the entire apparatus bulky, and increasing the difficulty of heat insulation, and, more important, the skill and time required to wind the flat coils. Such interchangers are therefore necessarily expensive. To obviate these difficulties Mr. George Nelson suggested on June 11, 1919, the use of short, twisted, flattened tubes in place of long ordinary tubes of the regular interchanger. The advantage of the flat tube over the round is that while the surface area of the tube is constant, the mean distance of heat flow is very much decreased, so that the efficiency of an interchanger, which for conditions of constant flow in grams per minute is proportional to area and roughly inversely proportional to the distance between walls, is greatly in excess for a flat tube than for a round tube of same area. The reason for twisting the tubes, as shown in A or B, Fig. 2, is to allow them to stand the high pressure without bulging.

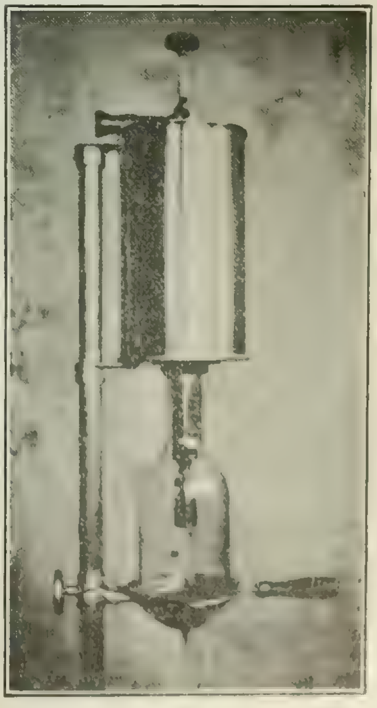

FIG. 3

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[3] Holborn and Jakob, *Z. Ver. deut. Ing.*, 58 (1914), 1429.

In the first experiments (November 8, 1919) there were used 15 in. of twisted tube, made by flattening down completely a section of three-sixteenth in. o. d. copper tube and twisting it uniformly on a lathe. In place of the elaborate expansion valve customary in liquefiers, various sorts of valves and orifices, the details of which are not important here, were used. Thermocouples were soldered on at the top, middle, and bottom of the twisted tube, in order to gain some idea of the thermal distribution. This tube was placed in a loosely fitting test tube insulated with cotton wool. The flow of gas used was about 0.2 cu. m. (6 cu. ft.) per min. The pressure was 220 atm. After thermal equilibrium had been reached, the temperatures of the tube at the top, middle, and bottom were, respectively, +20°, −5°, and −30° C., about what would be expected if there were no interchange. It was thought that this unfavorable result might be due to the fact that the flow outside the tube was not turbulent. Therefore the experiment was repeated, packing the space between the twisted tube and the test tube with coarse copper and aluminium powder. The temperature dropped very rapidly, and within 15 min. liquid air was observed in the bottom of the test tube, the temperature then being at the bottom −180°, at the middle −80°, and at the top +20° C. However, as the temperature of the outgoing gas was −10°, the efficiency of this interchanger was only 40 per cent of theory. In other experiments the aluminium powder was replaced by winding a spring of copper wire, as shown in Fig. 2-C. The efficiency for a 46-cm. (18-in.) interchanger at 0.2 cu. m. (6 cu. ft.) per hr. was 60 per cent. Several twisted tubes in parallel were also tried, and finally Mr. Nelson constructed a complete liquid air machine (Fig. 3), using 2 m. (6 ft.) of twisted tube in the interchanger. This machine had a capacity of 3.5 l. per hr. liquid air, using an intake pressure of 250, an intake temperature of 0°, and a free flow of air of 0.72 cu. m. (24 cu. ft.) per min., or an efficiency of about 70 per cent.

Such liquefiers would seem to have a great use for laboratory purposes. Their cost is but a fraction of the usual liquefier, their size is small (the height of the can in Fig. 3 is 12 in.), and as they use only 2 m. (6 ft.) of copper tubing for the interchanger, the time necessary to run the machine before it begins to form liquid air is much reduced, *i. e.*, 4 min. as compared with 30 min. or so for apparatus of the old type.

Interchangers using the twisted tube were also employed in a successful small-scale liquid hydrogen machine. The first designs of this machine (by Rodebush and Latimer and by the author) have, however, been superseded by a very ingenious design of Dr. Latimer's, which uses also the same twisted tube interchanger, and which will shortly be described by him.

CHANDLER MEDAL AWARD[1]

Introductory Remarks

By George B. Pegram
Columbia University, New York, N. Y.

It is our pleasure to be assembled this evening to hear as the Chandler Lecturer for the present year a gentleman who is widely known among chemists as a pioneer in the very remarkable developments of our knowledge that have been brought about through the study of food accessories such as vitamines.

I have the honor of introducing Professor Frederick Gowland Hopkins, of Cambridge University, England.

Medal Address

Newer Aspects of the Nutrition Problem

By F. Gowland Hopkins
Professor of Biological Chemistry, University of Cambridge, Cambridge, England

Nutritional Studies as a Branch of Applied Chemistry

The study of nutrition is most productive when it is followed as a branch of applied organic chemistry. As such it doubtless suffers certain disadvantages. It calls for workers fully acquainted with the technic of the chemical laboratory and possessed of all that is special in the chemist's mental equipment and mode of thought. Yet it calls for the application of these possessions in a region which is perhaps more remote from the chemist's experiences during his training than are any other of the many regions in which his science is applied. The successful pursuit of biochemistry, of which science nutritional studies form a part, calls for a second discipline. The young chemist having received his primary training must be content to become next something of a biologist; he must know enough about animals and plants to appraise the problems which their organization presents; he must acquire a biological outlook. Chemistry is a basal science underlying the practice of so many human activities that a large proportion of those who start with a chemical training must ultimately add to their equipment other kinds of expert knowledge before qualifying for their life's work. It is a pity that so few up to now have chosen biological qualifications. Hitherto, the primary training of most of those who have investigated biochemical problems has been biological or medical. Such workers have done very well, but as knowledge progresses it becomes more and more necessary that at least some of the work should be done by those whose chemical knowledge is primary and not secondary.

But I have referred to certain disadvantages suffered by biochemistry and you will think of one of them. It has hitherto been difficult to point clearly to a professional (as distinct from an academic) career for the young man who thinks of devoting himself to the subject. Only in connection with medicine has it hitherto offered professional opportunities, and medical qualification is often first demanded of its votaries. This state of affairs is rapidly altering. Medical practice can and will in the future be helped by workers whose training has comprised something less than a complete medical course. Biochemical knowledge, moreover, is being sought in many unexpected quarters. The scientific representatives of a firm that manufactures explosives on a great scale asked me some time ago to supply them with a biochemist. At first it seemed difficult to know why; but the explanation was simple enough. There is, or was, some anxiety about the supply of glycerol. Fats which used to be hydrolyzed are now being used intact in all sorts of fresh ways, and there is less glycerol as a by-product. Hence a desire to develop the methods by which it is produced by microörganisms, and the biochemist gets an opportunity. This is but one illustration. I can say with certainty that, in Great Britain at any rate, there is a demand for professional biochemists which is greatly in excess of the present supply. This I find satisfactory, for if a profession opens up we shall find it easier to obtain workers who during one period at least of their career will help advance the science itself.

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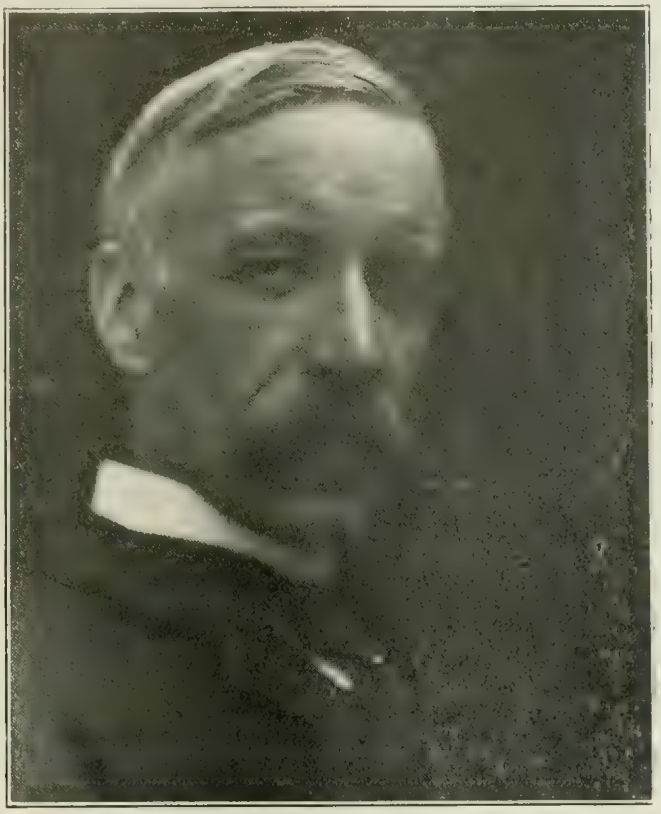
[1] Presented at Columbia University, New York City, April 18, 1921.

Need for Organic Chemists in Biology

I find it difficult, when addressing an audience composed largely of chemists, to avoid a propagandist attitude: because it is so very desirable that a proportion of our young chemists, greater than heretofore, should devote themselves to biological problems. I will confess that I am at the moment thinking in particular of organic chemistry. For it seems to me that on the whole the tendency has been for those who have especially qualified as physical chemists to devote themselves to biology rather than their colleagues who are more particularly accustomed to think in terms of molecular structure. Now no student of the plant or the animal can do otherwise than offer a hearty welcome to the physical chemist. He is now providing knowledge for which a whole generation of biological workers has been waiting. But if it be supposed that the application of the methods of physical chemistry, elegant and precise as they are, or the physical chemist's particular way of looking at things, is going to take us more directly and quickly into the secret habitation of life than other forms of chemical study; in particular if it be supposed that considerations of molecular structure are not essential to an understanding of living processes—then, I am sure, such suppositions are wrong.

In the main, though not of course exclusively, the physical chemist in biology is engaged in a study of the colloidal apparatus in which the dynamic events of life occur and in carefully and precisely defining a group of circumstances which conditions those events. We could, however, picture a physical system, composed of colloids similar to those which exist in the living cell, endowed with a characteristic structure, and in contact with electrolytes at a particular hydrogen-ion concentration, which would closely resemble a living unit when viewed from a purely statical standpoint; but unless what is ordinarily called metabolism occurs in such a system it is dead. Now metabolism consists in the continuous process of a set of organic chemical reactions in dynamic adjustment. Until our knowledge of these reactions and of their mutual relations is complete, our knowledge of living tissues will remain incomplete. This knowledge cannot come without continued thought and experiment on the lines of what we are accustomed to call organic chemistry. This applies to biochemistry as a whole, and not least to that branch of it which comprises the study of nutrition.



Professor Frederick Gowland Hopkins

There is of course one method of estimating the nutritional needs of the body which avoids consideration of chemical details. They may be dealt with from the standpoint of energetics. Indeed, as the last century closed, the facts of nutrition were coming to be viewed more and more exclusively from this standpoint. The criterion of an efficient dietary was apparently destined to be its caloric value, and, with one qualification, which seemed then to be lessening in significance, its caloric value alone. The chemical standpoint, in so far as it envisaged details, seemed to be losing its practical importance.

Successes and Limitations of Calorimetry

Those years saw a remarkable development in the technic of human calorimetry. The accuracy with which the energy exchanges in the body came to be measured gave rise in the minds of all students of nutrition to a sense of real accomplishment and to a feeling that, in addition to certain theoretical conclusions of great interest, calorimetry was making available, perhaps for the first time, information of a really quantitative kind to serve in practical guidance. The vague standards based upon statistical studies of the habits of the communities could at last, it was felt, be checked, and if need be corrected, by data which were in the truest sense scientific. What, in terms of energy, are the basal requirements of the body? What the caloric equivalent of various forms of mechanical work? What the efficiency of the human body as a machine? What the relative value of foodstuffs as sources of muscular energy? All these and kindred questions were being answered or the methods for their future solution made clear as the last century closed. They are, indeed, still being investigated, and with increasing accuracy, chiefly in the country where they were first seriously dealt with. For American workers, Graham Lusk, Benedict, Dubois and others are continuing the work of Atwater and Rosa, and are obtaining quantitative data which can be so controlled as to carry their own inherent proof of striking and even startling accuracy. The investigations are extending into the domain of pathological metabolism, and there I am convinced will have important bearings. Calorimetry as applied to human beings is an American science, and this country should feel the utmost pride in what it has accomplished. It is, in fact, impossible to overestimate the theoretical and practical importance of the data of human calorimetry. My only contention is that they are, and must always remain, insufficient for complete knowledge. In a limited sense calorimetry applies the methods of thermodynamics to the study of the body and its results share the advantage of conclusions reached by these methods in other branches of science. They involve quantitative statements which will remain true however our view may change with regard to the mechanism underlying those manifestations of change which permit easy measurement. The thermodynamic method is however sometimes like a blind man's stick. It carries us safely along a path which we cannot see, but fails to show us how we may best reach our ultimate goal. When there is complexity of a kind which cannot be reduced to statistics, the method of thermodynamics is apt to fail us. The human body obeys the laws of thermodynamics when, for this or that good reason, it is surely perishing!

Without, therefore, underestimating for one moment the value of thermal studies as applied to nutrition, I think it must be admitted that they in themselves can never constitute a sufficient guide for the progress of knowledge.

Importance of Structural Chemistry

Anyone, at any rate, who will trouble himself to appraise the nature of the progress which the detailed studies of the last twenty years have contributed to our views concerning animal and human nutrition will not doubt what I have said earlier as to the importance of thinking in terms of organic chemistry. Up to the end of the last century, thought about the chemistry of living beings scarcely employed considerations of molecular structure, or employed them, at any rate, in a very limited sense. Now, as the result of twenty years' progress, all concerned are doing their best to think in terms of structural chemistry; with the result that vague views about metabolism are giving place to clearer conceptions from which must follow a better understanding of the nutritive needs of the body.

Perhaps only those, who, like myself, have had to talk to students about such matters for five-and-twenty years, can fully realize how much the clarification of thought has progressed.

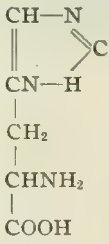
Modern Conceptions of Protein Metabolism

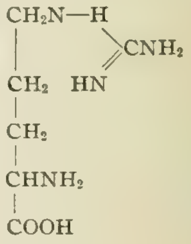
Especially, of course, is all this true in connection with the nutritive functions of protein. So long as we had to fit into our mental picture of what occurs in living tissues the hypothetical behavior of a complex molecule of which we knew little, and conceived of it as being oxidized, or otherwise utilized as a complex whole; oppressed therefore by the feeling that its very complexity would remove the processes involved from the domain of clear chemical presentation; so long as all this was the case we had to think in intellectual blinkers about the functions of protein. But simultaneously with the beginning of the present century, progressive work began which has changed the outlook. We have come to know that the complex molecule is built up of some twenty structural units, each a chemical species, but all belonging to the same chemical genus. We know the structure of each of these amino acids and realize that among them unity of type is combined with great diversity in structural detail, the unity and diversity being equally significant for the student of nutrition. We know, moreover, that the process by which we liberate these constituents from the protein complex in the laboratory—the process of hydrolysis—is identical with that which occurs in digestion. We know finally that in the alimentary canal this process is very completely carried out before adsorption of material occurs; so that the immediate phenomena of nutrition begin not with a supply of protein as such, but with a supply of amino acids. When we eat protein we consume, in effect, not one substance but twenty, and each of these may have quite special functions in nutrition. All-important to present and future progress is the fact that they are substances of known molecular structure. It is impossible, of course, for me to deal historically with this advance in knowledge. I have been instructed to narrate personal experiences, and though it may be unfair to others I will confine myself to illustrations drawn from such experiences.

I can claim that some eighteen years ago my imagination (doubtless like that of many others) was greatly stirred by the facts then becoming available. It seemed to me essential for the understanding of protein nutrition, and for the analysis of the factors concerned in the maintenance of nitrogenous equilibrium, that the relative nutritive importance and ultimately the precise fate of each individual amino acid should be determined separately. In 1906, in conjunction with Miss Edith Willcox (now Mrs. Stanley Gardiner), I published results of some experiments which illustrated the special nutritive importance of the indole nucleus contained in tryptophan, an amino acid first separated from protein a few years earlier by S. W. Cole and myself. Incidentally these experiments indicated that an amino acid may be used, not alone for the building up of tissue proteins, but also immediately and directly for more specific purposes. It is important when approaching studies of metabolism and nutrition to realize in advance that more than one path of change may lie before any particular unit in the food eaten. The results of the unambitious pioneer research just mentioned, in so far as it bore upon the importance of the indole nucleus, have since been confirmed by myself, and abundantly by others, on more conclusive lines. The fact recently demonstrated by Kendall, at Rochester, Minnesota, that the all-important active principle of the thyroid gland is an iodine derivative of indole has shown us one probable reason for the importance of a supply of tryptophan in the diet. This is only an illustrative instance of the special functions which may be subserved by individual parts of the protein molecule.

The circumstance that an animal can be normally nourished when, instead of intact protein, it receives a complete mixture of amino acids has greatly assisted studies meant to determine the relative nutritive importance of the different molecular groups in the protein molecule. The original amino acid mixture obtained by digesting any normal protein may be fractionated, and this or that constituent may be withdrawn from the mixture before it is supplied to the animal. Ultimately, by so withdrawing a particular unit and observing the effects of its withdrawal, we may not only measure its importance but also obtain information as to any special functions it may subserve.

I have myself tried the effects of withdrawing certain amino acids besides trytophan. If for instance an animal be given as its sole nitrogenous nutriment, the amino acid mixture deprived of hystidine and arginine, nutrition fails. It promptly becomes normal again when these two units are restored to the food. The first of these substances contains the iminazole ring, and the second gets its special stamp from the existence of the guanidine group in its molecule. Now it is remarkable that, though the absence of both these amino acids from the food supply is fatal, the absence of either alone is well borne by the animal, and experiment shows that one can take the place of the other in metabolism. Considerations of molecular structure make it easy to understand why this may well be the case and the body in this case clearly takes advantage of certain possibilities which are obvious to the chemist.


Histidine


Arginine

Similarly a deficiency of tyrosine may be compensated by a larger supply of the closely related phenylalanine; and there are probably similar cases. Such facts help to throw light upon the equipment of the tissues as laboratories: they must also be borne in mind when we are estimating the nutritive value of any particular form of protein.

Considerations of molecular structure made it probable that arginine and histidine might well be the precursors of the purine bases which are characteristic constituents of the nucleic acids found in all tissue cells. Led by the structional suggestions, Ackroyd and the writer some years ago tested this matter by feeding experiments, and obtained evidence to show that the suggestions were fulfilled. Arginine and histidine seem to be the special raw material for the synthesis of purines in the body.

On the other hand, there are constituent groups in protein which are certainly of much less nutritive importance than those discussed. Especially would this seem to be true of those amino acids which have a relatively simple constitution—the aliphatic substances, for instance, with a normal chain of carbon atoms. I have myself found, for instance, that if glutamic acid, aspartic acids, and hydroxyglutamic acid recently identified by Dakin be all removed from the amino-acid mixture, animals can maintain themselves quite well upon the residual amino acids. The contrast between the fatal effects of removing tryptophan, which constitutes some two per cent only of a normal protein, with the almost negligible effects of removing the amino acids just mentioned, which may represent perhaps thirty per cent of the protein, is sufficiently striking. There is little doubt that the difference is due, not to the fact that the tissues can dispense with any protein constituent necessary to their normal chemical make-up, but rather to the range of synthetic possibilities within the body. When deprived of a supply of certain amino acids, it can synthesize them for itself; the synthesis of others is not within its powers.

Very interesting is the knowledge, incomplete as yet, which we possess concerning the chemical changes which individual amino acids actually undergo in the body. The fate of each is individual because its molecular structure is individual. I could indeed better illustrate the truth of my opening contention concerning the importance of structural considerations in biological chemistry if we were considering intermediary metabolism rather than nutrition in the more limited sense. The few facts I have put before you will, however, illustrate it sufficiently.

The outcome of the recent advances in knowledge concerning the chemistry and metabolism of protein when viewed from the standpoint of practical dietetics is in the main this: We cannot any longer be content to speak of the body's demands for "protein" in unqualified terms. The balance of individual amino acids, the relative amount of this or that acid, may be, we know, very different in different proteins, and this difference may markedly affect the relative nutritive value. For the future we must in this connection think of quality as well as quantity.

What we know about the functions and fate of the other basal foodstuffs, the carbohydrates and fats, illustrates equally well the importance of structural considerations in biochemistry. But with these I cannot deal.

VITAMINES

I will rather pass at once to a newer aspect of our knowledge concerning the nutritional demands of the body, and remind you of facts which more than any others illustrate the necessity, when we are seeking to define an efficient dietary, of considering the nature of the material, as well as the energy supply. I mean, of course, the facts concerning the accessory food substances, as I once ventured to name them, or (to use the more familiar name conferred on them by Casimir Funk) vitamines. As you are doubtless aware, the chemical nature of these substances is as yet unknown. Their properties cannot therefore at the moment be used to illustrate further my theme concerning the importance of molecular structure in nutritional phenomena, though I doubt not that once they are isolated the biochemist will have an interesting task in relating their action to their structure. But there are other reasons why I should speak to you concerning them. I have received credit—perhaps too much credit—as pioneer in their discovery. Ten years ago the time was ripe for the emergence of certain facts. They were in the air; and when, in the progress of science, this is the case, questions of priority lose their importance. I will however relate my own experiences.

During 1906 I was engaged in feeding animals upon mixtures of different amino acids, and of necessity had to employ synthetic foods. Starch, fats, and salts were added to the amino acids to complete the dietary. The first circumstance which set me thinking was the observation that animals prospered better when they were fed upon amino acids obtained by fully digesting *tissues* than when the source of amino acids was a separated and purified protein digested in the same way. Lean beef, for instance, gave better results than casein. At first one was inclined to attribute the differences either to the fact that the amino acid balance was better in the former, or to the presence in the tissues of familiar substances, such as lecithin, but I could not get confirmatory evidence for this supposition. The first strong suggestion that something special had to be looked for came not from my main experiments, but from their controls. In the latter the animals were, for the sake of comparison, given intact casein instead of the amino-acid mixture, the rest of the diet being the same. Now, for a long time these control animals grew very well and kept in good health. If growth was slow I put it down to the fact that a synthetic diet might in any case be somewhat unsuitable for an animal. From a certain date onward, however, all the animals on casein began to do badly. They showed no growth at all and their health failed. After some time the reason occurred to me. For the preparation of amino acids I used pure casein, but for the food of the control animals a commercial article was used. On the date referred to I had begun to feed these animals on a casein preparation different from that which for a long time previous had served as the protein supply of my laboratory. The new preparation had just come on the market and in appearance seemed a much better article; but there was soon no doubt that its use was the cause of the failures. When put upon the old casein supply all the animals grew again!

At first I was naturally inclined to think that the new protein had suffered some sort of denaturation during the course of its manufacture, but that supposition suffered easy disproof. When, earlier, I began experiments with synthetic diets I added small quantities of meat extracts and extracts from yeast to give flavor to the tasteless food. I was thinking then of the animal's "appetite," as was natural, and as most people do when they start such experiments. I quickly found, however, that rats ate synthetic diets very well without such additions, and at the time of the experience with casein just mentioned I had ceased to use them. Nevertheless my memory at this time, if not my notebooks, carried suggestions concerning the influence of the extracts which led me to try adding them to diets containing the new casein, with striking results. Growth was now as good, and sometimes better than with the old casein, and growth occurred, too, in animals which were eating no more, or even less, than other individuals living on the pure casein diet without addition and showing continuous loss of weight as a result. The extracts powerfully affected nutrition. I now extracted the old casein with various solvents and finally got a product which behaved exactly like the new. When the substances dissolved out were returned to the food, growth occurred as before.[2] I wasted a good deal of time by trying the effect of various familiar substances of determined nature known to be in yeast; always with unsatisfactory results.

By this time I had come to the conclusion that there must be something in normal foods which was not represented in a synthetic diet made up of pure protein, pure carbohydrate, fats, and salts; and something the nature of which was unknown. Yet at first it seemed so unlikely! So much careful scientific work upon nutrition had been carried on for half a century and more—how could fundamentals have been missed? But, after a time, one said to oneself, "Why not?" The results of all the classical experiments had been *expressed* in terms of the known fundamental foodstuffs: but these had never been administered *pure!* If, moreover, the unknown, although clearly of great importance, must be present in very small amounts—again, why not? Almost infinitesimal amounts of material may have a profound effect upon the body, as pharmacology and the facts concerning immunity assure us. Why not then in nutritional phenomena? The animal depends ultimately upon the plant for the synthesis of materials which bulk largely in its food: there is no reason why it should not be adjusted so as to be in equal need of substances which the plant makes in small amount. Only if energy were the sole criterion of an animal's needs would this be impossible; but certainly it is not the sole criterion.

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[2] It is remarkable what a considerable proportion of the vitamines present in milk is adsorbed by precipitated casein. A failure to recognize this has often obscured the results of feeding trials.

So my faith grew in the existence of a previously unrecognized type of nutrient.

At this period I spent much time in the endeavor to isolate from yeast extracts an active substance with definite chemical properties, but wholly without success.

The experimental period that I have been describing was, for me, in one particular, unfortunate. I experienced periods of continuous success in maintaining growing animals upon purified dietaries after the addition of very small quantities of fractionated yeast preparations, but they were interspersed with occasional failures which shook my confidence. Only when milk, in small amounts, formed the addendum did failure never follow. The explanation is now clear. The protein and carbohydrate used in my experiments were thoroughly purified and standardized, but for fat I used lard. But lard, as many experimentalists now know to their cost, is a variable fat. What I was adding or witholding in my early experiments was vitamine B alone. I taught myself nothing about vitamine A, which is associated with most animal fats. The amount of it in commercial lard varies greatly; and I have no doubt that when my animals did well the lard they consumed contained enough of it; while when they did ill the lard was deficient in this particular.

I was on safer ground in using milk, for though milk is not especially rich in vitamines it always contains both A and B. When, therefore, at last, I ventured on publication it was mainly my experiments with milk that I described in proof of the existence of accessory food factors.

A great step forward was made in 1913 when McCollum and Davis made it clear that there are at least two vitamines—those just mentioned—concerned in nutrition; for we have since learned how great is the nutritive importance of fat-soluble A, of which the existence was then demonstrated. It seems to me fair to say that a recognition of the importance of a factor associated with fats was implicit if not explicit in papers published at this time by Osborne and Mendel, and their experiments in proof of this appeared close on the heels of McCollum's now classic publication. Such fundamental matters could not indeed long escape the organized and intensive work which was being done at the American centers of activity.

I have given you a brief account of my own early experiences in this domain (never having told about them before) because I was assured that you would care to hear it. I fear you may have found it trivial, though the period it deals with contained some thrilling moments for me.

It would have been more useful, I imagine, if I had attempted to give you a critical appraisement of the present position of our knowledge of vitamines. To attempt one now would be unwise, for to be of use it would take much time. Advances have been real during the last year or two, but chiefly in matters of detail. Perhaps no considerable advance can now occur until a vitamine has been isolated in pure form and its constitution determined. I am sure that this will be no very distant accomplishment.

If indeed there be any in this audience who feel skeptical with regard to the whole question of vitamines or at any rate with regard to their practical importance (there are still some skeptics in my own country!), I feel that I am qualified to ask them to reconsider their attitude. Apart from the many hundreds of experiments I have made myself, I have seen the work which is being done upon the subject at some of the chief centers of activity. I can testify to the care and effort which is being put into the study at the Lister Institute and at University College, London. I have recently paid illuminating visits to the departments of Drs. Osborne and Mendel at Yale, and to that of Dr. E. V. McCollum at the Johns Hopkins University. In each and all of these centers one finds thorough organization and a properly critical atmosphere. The technic used in the study of vitamines has now been developed till, in its own special way, it is exact and reliable. All concerned have to talk and write under the disadvantage which arises from the fact that the actual nature of these substances remains unknown, but in spite of this a great amount of real knowledge of practical value is being accumulated.

Between the experiments on animals and actual human experience there are, as you know, links enough. The absence of one particular vitamine from the food is the whole and sufficient reason for the occurrence of human scurvy, the absence of another forms the main factor in the etiology of a second disease, beriberi, the absence of a third plays at least a large part in the induction of rickets. But if extreme deficiency in such factors results in actual disease, who shall say how much vague ill health may follow upon relative deficiency? That is the consideration which gives importance to this newest chapter in the science of nutrition.

While the newer knowledge which has grown up on the lines that I have briefly and incompletely indicated has undoubtedly important practical bearings, those engaged in the work should doubtless use caution in their relations with the public. We should keep a sense of proportion. It would be wrong, for instance, or so it seems to me (I have heard the contrary opinion expressed) so to exaggerate the importance of the fat-soluble vitamine as to teach that vegetable fats which do not contain it should disappear from the market. Fat, as such, is after all a valuable and necessary food of which it is none too easy to maintain a supply. We should rather show how such fats are to be supplemented properly whenever they form a considerable part of the public supply.

Again, although there can be no doubt that the fundamental phenomena of nutrition are the same in all mammals, there are specific differences which we should not forget in applying our laboratory results. Deficiencies are felt more immediately and directly by the small animals on which so many of our experiments are done than by larger species with slower metabolism. We may consequently tend to exaggerate the general importance of this or that factor. We should not, I fancy, make too much of the "biological value" of proteins in connection with human nutrition until more observations have been made upon human subjects. The most favorable balance of amino acids may be different in different species; though as a matter of fact the weight of evidence is against this possibility. At any rate, we must remember that physiological adjustments may be made during long periods of use and custom which could not occur during the relatively brief duration of an experiment. In connection with the part that food deficiencies may play in the causation of human diseases, we should bear in mind that a clinical condition is usually more complex than conditions observed in the laboratory as the result of varying a single factor.

Nevertheless, as I have already said, there exist many links of evidence to show that laboratory results are fully paralleled in human experience, and evidence of this sort tends to increase. There is at any rate no fear of exaggerating the importance of the newer outlook when the rearing of children is in question. If one had to sum up in a sentence what constitutes that newer outlook, I would say that it is a fuller recognition of the fact that quality is as important as quantity in all that concerns nutrition. But "quality" must be read in a new sense, a sense sufficiently defined by the facts I have been discussing.

I referred earlier to the literal fact that human calorimetry is an American science. It seems to me as I think of those who are engaged in the study of nutrition on the fresh and extended lines that, unless we who work elsewhere work very hard, the new science which is developing will come into the same category.

Presentation of Chandler Medal

By George B. Pegram
Columbia University, New York, N. Y.

There are certain names that stand for whole periods in the existence of institutions, epitomize epochs of development and accomplishment. No such name at Columbia stands for more than Chandler. Reaching from the foundation of the School of Mines in 1864 to the present and covering nearly half a century of labor and responsibility in active connection with the development and progress of scientific work at Columbia, his great personality has built itself into the structure of this University in so intimate a fashion that the keenest analysis could not separate it out. It was, therefore, a most appropriate action for a group of his friends to present to the Trustees of Columbia University a sum of money constituting the Charles Frederick Chandler Foundation, the income from which is to be used to provide each year a lecture by an eminent chemist and to provide a medal to be presented to the lecturer in public recognition of his achievements in science. The previous lecturers on this Foundation have been L. H. Baekeland, Sc.D., W. F. Hillebrand, Ph.D., and W. R. Whitney, Ph.D.

On the recommendation of a University committee, the Trustees of Columbia University have awarded the Chandler Medal for this year to Frederick Gowland Hopkins, F.R.C.P., F.R.S., F.I.C., F.C.S., Fellow of Trinity College, Honorary Fellow of Emanuel College, Cambridge, Member of the Medical Research Council, and of the Consultative Council to the Minister of Health, Professor of Biological Chemistry, Cambridge University.

Professor Hopkins, this medal is presented to you in public recognition of your pioneer and valuable researches in biochemistry, particularly in connection with food accessories, such as vitamines, and your public service on the Medical Research Council and the Consultative Council to the Minister of Health.

ADDRESSES AND CONTRIBUTED ARTICLES

Contribution to the Theory of the Water-Gas Process[1]

By S. Kohn
Rohm & Haas Co., Inc., 40 N. Front St., Philadelphia, Pennsylvania

The usual explanation of the interaction between steam and carbon is that at about 600° C. carbon dioxide and hydrogen are the chief products formed, according to the equation

$$C + 2H_2O = CO_2 + 2H_2 \qquad (A)$$

and that, as the temperature rises, more and more carbon monoxide appears in the resulting gases. Finally, at about 1000° C. and above, carbon monoxide and hydrogen are practically the sole constituents of the gases, which may conceivably be formed according to the equation

$$C + H_2O = CO + H_2. \qquad (B)$$

At temperatures between 600° and 1000° C., both reactions may be considered as taking place simultaneously.

The standing of Equations A and B, as an explanation of the chemistry of the water-gas process, is that of a fairly useful hypothesis. We have no proof that the reactions actually proceed in the manner indicated. Furthermore, while these equations do explain satisfactorily some of the phenomena, they are not sufficient to explain all. Haber,[2] after introducing and discussing Equations A and B, adds: "Now one can consider that A and B are also connected by the equation

$$C + CO_2 \leftrightarrows 2CO,"$$

and he uses this third equation for further elucidating the peculiar relations between the volume concentrations of the resulting gases in the water-gas process. Rideal[3] thinks that the following combination of three equations represents the chemistry, of the water-gas process:

$$\begin{aligned} &C + H_2O = CO + H_2 \\ &CO + H_2O \leftrightarrows CO_2 + H_2 \\ &C + CO_2 \leftrightarrows 2CO \end{aligned}$$

These instances will suffice to prove that our present conception of the chemistry of the process is open for discussion, and that each investigator is wont to call upon such a set of two or three equations as may seem to him necessary and sufficient to depict the reactions and explain the results obtained.

As will be shown below, ten sets of equations are theoretically possible. This number will be reduced to three by making a certain assumption, and it will also be demonstrated that the analysis of the resulting gases, in the cases under observation, not only supports the assumption made but also contains a definite clue as to which of the three sets of equations represents the actual procedure of the reactions.

Possible Reactions of Steam and Carbon

When steam reacts on carbon, carbon dioxide, carbon monoxide, and hydrogen are formed (we shall ignore here the formation of small amounts of methane and other hydrocarbons), and all possible interactions between the steam and carbon and the resulting three gases are represented by four reversible equations:

$$\begin{aligned} &C + 2H_2O = CO_2 + 2H_2 && (A) \\ &C + H_2O = CO + H_2 && (B) \\ &CO_2 + H_2 = CO + H_2O && (C) \\ &CO_2 + C = 2CO && (D) \end{aligned}$$

It may happen that reactions according to all four equations occur simultaneously (A, B, C, and D) or that under certain conditions only the four possible combinations of three will assert themselves, and finally we can think of the possibility of either one of five possible pairs of equations representing the actual procedure, that is, A and B, A and C, A and D, B and C, and B and D.

If we consider, however, that there are indications that carbon monoxide is not formed by the direct oxidation of carbon[4] but that carbon dioxide is formed primarily and the occurrence of carbon monoxide in the gases is to be ascribed to a secondary reduction of CO_2 to CO by means of hydrogen or carbon, the ten combinations enumerated above dwindle to three, namely, A and C, A and D, or A, C, and D. That is to say, the chemistry of the water-gas process most probably consists of two consecutive steps: first, carbon dioxide and hydrogen are formed from steam and carbon, and, second, the dioxide is reduced to monoxide either by hydrogen or by carbon or by both hydrogen and carbon simultaneously.

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[1] Received August 3, 1921.

[2] "Thermodynamik technischer Gasreaktionen," 293.

[3] *J. Soc. Chem. Ind.*, **40** (1921), 131.

[4] Haber, *Loc. cit.*, 238.

The main object of this paper is to answer the following questions:

> Do the differences in the manner of working of Schemes A and C, A and D, and A, C, and D make themselves felt in the composition of the resulting gases?
>
> If so, how can we use these differences to determine whether a gas of given composition has been the result of the first, second, or third combination?

Relations between Volumes of Gases

Before going into this matter, the relationship between the volumes of H_2, CO, and CO_2 will be shown by utilizing one of the pairs of equations which have been dropped as practically improbable but which remain, of course, theoretically correct and useful. The pair chiefly used in textbooks is A and B. It probably does not represent actual working conditions for several reasons, but its merit lies in its clearness and in the fact that the two reactions proceed parallel and not in series. However the water-gas process actually proceeds, it is theoretically correct to say that the resulting gases could have been formed according to these two reactions. Certain general characteristics of the process can be deduced from them more easily than from any other. One of these characteristics of which we shall make repeated use in the following calculations lies in the fact that the volume of hydrogen is always equal to the sum of the volume of carbon monoxide plus double the volume of carbon dioxide. If we call X, Y, and Z the respective concentrations by volume in the end gases of CO_2, CO, and H_2 we can say that

$$Z = Y + 2X. \qquad \text{(E)}$$

Equation E also indicates that, for a given value of any one of the three gases after removal of the excess of steam, only one set of values for the other two gases is possible. For instance, if X is given or determined, Y and Z can be calculated as follows:

$$Y = \frac{100-3X}{2} \text{ and } Z = \frac{100+X}{2} \qquad \text{(F)}$$

Equilibrium relations—Returning now to the problem of determining the direction which the reaction has taken by the analysis of the resulting gases, the first advance in attacking this problem has been made by recognizing the apparent impossibility of utilizing the law of reaction equilibrium for this purpose. The equilibrium of the resulting gases with each other and with the carbon, that is, the equilibrium represented by the two following equations, is in the first instance only exceptionally obtainable; in the second, as a rule, not even approximately reached.

$$\frac{U\,Y}{X\,Z} = K$$

$$\frac{Y^2}{X} = K_1$$

X, Y, and Z are again the volume concentrations of CO_2, CO, and H_2, and U is the volume concentration of the unconsumed steam.

The explanation of the failure of these equilibria to establish themselves under ordinary working conditions lies in the fact, proved by experiment, that even if the observations are started with definite amounts of, say, CO_2 and H_2, which are not changed from the outside, it takes a longer or shorter time, depending on conditions, for the equilibrium to assert itself. If then, as is the case in the water-gas process, one of the gases is continually introduced in new quantities, we can hardly be surprised that the equilibrium can never be reached.

Evidently if the two reactions under observation are not working in parallel, and if the second is dependent upon the reaction products of the first, we must look for other means to detect the law of interdependence. Considering the fact that the first step produces CO_2 which the second uses for the production of CO, it is to the point to endeavor to find the relationship between the rate of production of CO_2 by the first step and the rate of destruction of CO_2 by the second step; or, what amounts to the same thing, between the rate of decomposition of water by the first step and the rate of decomposition of CO_2 by the second step. Further, if the combination A and C works differently from A and D, these differences will show themselves in the end gases and permit answering the problem.

Equations A and D—Let us consider first pair A and D, as the simpler one, taking as a basis one volume of steam before it is decomposed. Assuming that under given conditions of temperature, etc., fraction p of the steam used has been actually decomposed by interaction with carbon according to A, and that fraction q of the formed CO_2 has been reduced to CO according to D, the volumes of the four resulting gases will be proportionate to the following values:

Undecomposed steam $= 1-p$
Hydrogen $= p$
Carbon monoxide $= pq$
Carbon dioxide $= \frac{p}{2}(1-q)$

While it is evident enough that p is equal to $\frac{Z}{U+Z}$ we cannot call q equal to $\frac{Y}{X+Y}$, because, as Equation D shows, the volume of the CO_2 doubles by the change to CO. As the rate of reaction will depend on the volume concentration of the CO_2 during the reaction and not after the reaction, we must make

$$q = \frac{\frac{Y}{2}}{X+\frac{Y}{2}} \quad \text{or} = \frac{Y}{2X+Y}$$

Equations A and C—Conditions are slightly more complicated with pair A and C. This combination differs in two respects from A and D:

(1) One volume of CO_2 produces only one volume of CO and we can therefore put $q = \frac{Y}{X+Y}$.

(2) Equation C reproduces one volume of steam for each volume of CO_2 used up.

In order to finish our observations again with p volumes of water decomposed and $1-p$ undecomposed, we must start our observations with a large volume of steam initially decomposed by Reaction A, which we shall call P. P can be determined by the following equations:

$$1 - P + \frac{P.q}{2} = 1 - p \qquad \text{(G)}$$

$$P = \frac{2p}{2-q}$$

If then $\frac{2p}{2-q} = P$ water is decomposed according to Equation A, $\frac{P\,q}{2} = \frac{p.q}{2-q}$ water is reproduced according to Equation C. This is the same as if only p water had been decomposed and $1-p$ had been left undecomposed, and the four gases after the reaction are again represented in the following proportions:

Undecomposed steam $= 1-p$
Hydrogen $= p$
Carbon monoxide $= \frac{pq}{2-q}$
Carbon dioxide $= \frac{p\,(1-q)}{2-q}$

If the second step depends on the formation of CO_2 by the first step (and on the other hand, the rate of formation of the CO_2 will be dependent on the rate at which it is removed by the

Observation	(1) T ° C.	(2) H_2 (Z)	(3) CO Y	(4) CO_2 X	(5) H_2O U	(6) Flow Liters Sec.	(7) K Observed	(8) K Calculated Luggin	(9) Y + 2X = Z	(10) p	(11) q_d	(12) q_c	(13) $\frac{Y}{X}$	(14) $\frac{Z}{U}$
I	674	8.41	0.63	3.84	87.12	0.9	1.70	0.49	8.31	8.8	7.53	14.1	0.164	0.0965
II	758	22.28	2.67	9.23	65.82	1.8	0.85	0.70	21.13	25.3	12.6	22.4	0.289	0.339
III	838	28.68	6.08	11.29	54.00	3.65	1.01	0.98	28.62	34.7	21.1	34.8	0.536	0.531
IV	838	32.77	7.96	12.11	47.15	3.28	0.94	0.98	32.18	41.0	24.7	39.8	0.659	0.695
V	861	36.48	11.01	13.33	39.18	5.3	0.89	1.07	37.67	48.2	29.3	45.2	0.835	0.930
VI	954	44.43	32.70	5.66	17.21	6.3	2.25	1.41	44.02	70.2	74.2	85.2	5.77	2.58
VII	1010	47.30	48.20	1.45	3.02	6.15	2.12	1.65	51.01	94.0	94.0	97.0	33.2	15.7
VIII	1060	48.84	46.31	1.25	3.68	9.8	2.78	1.88	48.81	93.0	94.8	97.4	37.0	13.3
IX	1125	50.73	48.34	0.60	0.303	11.3	0.48	2.11	49.54	99.4	99.9	100	80.5	167.0

second step), the equilibrium between these two reactions working in series will be established if q equals p. For, assuming that at the very beginning of the reaction q does not equal p, the higher rate of decomposition of one of the two gases will enhance the rate of decomposition of the other gas by increasing its volume concentration and at the same time reduce its own rate of decomposition by decreasing its own volume concentration. Equilibrium will be quickly established, and the rate of decomposition of steam will become equal to the rate of decomposition of CO_2. The shortest adequate mathematical expression for this fact is

$$q = p.$$

In this case we have the desired criterion as to whether the reaction has proceeded after A and C or A and D in the following simple relations:

$$\frac{Y}{X} = \frac{2p}{1-p} = \frac{2q}{1-q} \text{ for the combination AD}$$

$$\frac{Y}{X} = \frac{p}{1-p} = \frac{q}{1-q} \text{ for the combination AC}$$

$$\text{or} \quad \frac{Y}{X} = 2\frac{Z}{U} \qquad \text{(H)}$$

$$\frac{Y}{X} = \frac{Z}{U} \qquad \text{(I)}$$

U stands here for the volume percentage of undecomposed steam in the resulting gases.

Application to Bunte-Harries Observations

The application of these deductions has been tried out on the series of nine observations made by Bunte–Harries. To the table of Harries, which after the recalculations and additions by Luggin[5] amounts to the first eight columns of the accompanying table, we add a Column 9 marked Y + 2X. This indicates the degree of analytical accuracy of the gas determinations. In most cases the values given under Y + 2X check very well with the values for hydrogen. Column 10 contains the quotient of decomposition of the steam in per cent, as given by the original Harries table. Columns 11 and 12 give the q_c and q_d, respectively, meaning the quotient of decomposition of CO_2 by Equations C and D, respectively.

If in this table we consider the fact that the last two or three observations are of minor accuracy on account of the very small value for CO_2 and steam, and the fact that p and q are very near 100 per cent, we are surprised to find that p is always very nearly equal to q_c or q_d and never shows values between the two decomposition factors of CO_2. This can mean only that in the cases observed the equilibrium between the first and second reactions has always been very nearly established, and that if for any reason the Reaction C was favored against the Reaction D, the equilibrium by this reaction was so quickly reached that the D reaction was left far behind, or vice versa.

Columns 13 and 14 show $\frac{Y}{X}$ and $\frac{Z}{U}$, respectively (see Equations H and I). It is surprising to find the indications in Observations II, III, IV, and V for the pair AC, and in I, VI, and probably VII for the pair AD (Observation I should probably not be given too much weight as pointing toward AD, because of the low CO figure). Differences of working conditions may have been responsible (such as different quality of carbon or different size of the charcoal pieces), or it also may be that there is always (even under strictly comparable working conditions) a sudden turn in favor of AD around 900° C. For Reaction C is endothermic and therefore favored by increased temperature, but the enhancing influence of a rise in temperature diminishes, the higher the temperature climbs, and this may be responsible for the sudden turn around 900° C. The table also explains why "K observed" does not check with "K calculated." From Equations H and I, we can calculate that "K observed" will equal 1 or 2, depending upon the course of the reaction. Excepting in Observations II and VII, where a comparison of Columns 2 and 9 shows that the analytical errors were considerable, the fact that Equations H and I are not more perfectly satisfied can be taken as an indication, where the values for $\frac{Y}{X}$ are too high, of a direct formation of some CO, without the intervention of CO_2, in accordance with the proposed existence of a primary complex C_mO_n. As can be seen, however, the part played by this complex would amount to only a small fraction of the total sum of reactions.

Similar calculations as outlined for AC and AD lead to the following equation for BC and BD:

$$\frac{Y}{X} = \frac{U}{Z} \quad \text{for BC}$$

$$\frac{Y}{X} = 2\frac{U}{Z} \quad \text{for BD}$$

This is, in view of the above table, a direct proof that the Reaction B did not occur. As to AB, this pair of equations shows only a different way of writing AD. The resulting gases would only then indicate a possibility of the reactions proceeding according to AB if no such relations as H and I call for were observed. Since A and B are working independently of each other, only the more general interrelations given by Equation G would have to be satisfied.

Application to Selective Action of Catalysts

It is interesting to note what light these observations throw on the assumed selective influence of certain catalysts. As can be seen, a catalyst which increases the velocity of C or D will most probably also automatically increase A. But there may be some catalyst which will increase C without being effective on D. Such an instance is cited by Rideal[6] as a suggestion of Haber, but the figures of Gwosdyz cited later are not in keeping with such an assumption. Rideal gives only the CO_2 percentages of two experiments by Gwosdyz[7] and says: "A coke containing 8.5 per cent ash yielded 29 per cent CO_2, while pure carbon (lampblack, 0.1 per cent ash) yielded only 8.6 per cent CO_2 at 560° C." If this means percentages in the dry gases, we can figure out with the aid of Equation F that in the case of coke the gas analyzed 29 per cent CO_2, 6.5 per cent CO, and 64.5 per cent H_2, and in the case of lampblack 8.6 per cent CO_2, 37.1 per cent CO, and 54.3 per cent H_2; from this, one would conclude that the greatly enlarged surface of the lampblack greatly expedited Reaction D, as otherwise the high percentage of CO would be unexplainable at this temperature. On the other hand, the composition of the gas in the other instance is about what would normally be expected at 560° C., and explanation on a basis of the ash content of the coke seems superfluous.

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[5] Haber, *Loc. cit.*, 121.

[6] *J. Soc. Chem. Ind.*, **40** (1921), 141.

[7] *Z. angew. Chem.*, **1918**, 137.

If the amount of undecomposed water had been given, we could draw more definite conclusions about just what happened in those two cases, although a high carbon monoxide content at low temperature is always pointing toward combination AD.

SUMMARY

1—The ten possible and three probable combinations of reactions which can be called upon to explain the water-gas process are discussed.

2—Demonstration is made of a possibility of drawing conclusions from the composition of the resulting gases to the actual procedure of the reactions.

3—The applicability of the principles outlined is tested on a series of nine observations published by Bunte and Harries.

4—The application of these considerations to catalytic observations is discussed.

The Latent Heat of Vaporization of Coal-Tar Oils[1]

By **John Morris Weiss**

THE BARRETT CO., 40 RECTOR ST., NEW YORK, N. Y.

Some time ago W. J. Huff[2] published the results of work carried on in our laboratories on the vapor densities of coal-tar fractions. It has since proved desirable to have some knowledge of the latent heats of vaporization of these fractions, and we have found that the latent heats can be calculated from the vapor densities with a fair degree of accuracy.

According to the principles of physical chemistry, the quotient obtained by dividing the molecular heat of vaporization by the boiling point (expressed as absolute temperature) is an approximate constant for normal substances. This is known as "Trouton's Rule." This relation was later critically examined by Nernst and the formula changed so as to make it of more rigid application.

Let T = absolute boiling point and
M = the molecular heat of vaporization

Then Nernst's revised rule of Trouton is

$$\frac{M}{T} = 9.5 \log T - 0.007\,T.$$

In this expression M is defined as the "amount of heat in gram calories required to vaporize 1 g. molecule of the substance." From this formula, given the molecular weight of a material and its boiling point, we can readily calculate its heat of vaporization by dividing M by the molecular weight.

Certain substances do not conform entirely to this law. This apparently includes materials which are considerably polymerized in the liquid state but which possess normal densities in the gas state. With coal-tar compounds, however, there is no evidence of any such association in the liquid state and it seems safe to conclude that the latent heat of these materials can be obtained accurately by calculation. It is somewhat interesting to note here a comparison between actually determined latent heats and calculated latent heats according to the revised rule of Trouton. The basic data are taken from Landolt-Börnstein, Section 185.

	Boiling Point ° C.	Latent Heat of Vaporization Calories per Gram	
		Determined	Calculated
Pyridine C_6H_5N	115	101–104	107.5
Toluene $C_6H_5CH_3$	110.8	83–87	91.4
m Xylene $C_6H_4(CH_3)_2$	139.9	78–82	85.5
p-Xylene $C_6H_4(CH_3)_2$	138.5	80–82.5	85.3
Benzene C_6H_6	80	93–95	98.2
Turpentine $C_{10}H_{16}$	159	68–74	69.9
m-Cresol $CH_3C_6H_4OH$	201	100.4	97.1
Cyclo-hexane C_6H_{12}	80	85–87	91.2
Octyl alcohol (normal) $C_8H_{17}OH$	196	79–5	79.7

This shows clearly the difference which might be expected between the calculated latent heat and that obtained by actual experiment, and it is evident that the error in the majority of cases would not be more than 5 per cent. It is in fact probable that the calculated latent heats are more nearly correct than those obtained experimentally because of the technical difficulties of latent heat calorimetry.

We have similarly calculated the latent heats of oil fractions, using as our basis the vapor densities determined by Huff, and in the higher fractions have naturally transposed the boiling points under the reduced pressures to correspond approximately to the lighter fractions which were taken under normal pressures. In addition, we have extrapolated the last fraction so as to obtain some idea of the latent heat of vaporization of materials above 440° C. boiling point.

FRACTION	Temperature Range ° C.	Vapor Density Grams per Cc. at Normal Temperatures and Pressures	Molecular Weight	Heat of Vaporization, Cal. per G.
I	199–249	0.00578	129.5	84.8
II	249–296	0.00667	149.5	81.0
III	296–345	0.00691	154.8	85.1
IV	345–392	0.00867	194.2	73.3
V	392–438	0.01047	234.5	65.1
Assumed	438–488	0.011–12	257.5	63.1

It is to be regretted that the writer has been unable to find authentic data on the latent heats of materials such as naphthalene and anthracene to check the oil fractions further with experimental data of substances which have similar boiling points. It is believed, however, that the results are accurate enough for all practical purposes and that they may be useful as an addition to the known constants of these rather complicated mixtures, the coal-tar distillates.

Science in Verse

Dr. C. E. Ruby has in preparation an anthology of scientific doggerel, which will probably be entitled "Jingles in Science." In order to make this collection of scientific nonsense in verse as complete as possible, and as entertaining as possible, readers are invited to send any verses or limericks dealing with the sciences to Dr. Ruby, 7 St. Paul St., Cambridge, Mass.

Seventy-one companies with an authorized capital of $50,000 or greater were organized during the month of November 1921 to engage in some branch of the petroleum industry, involving a total indicated investment of $60,129,000. This is an increase in number of companies but a decrease in total capitalization, as compared with October 1921, which showed 55 companies with a capitalization of $83,450,000. In November 1920, the total capitalization was $266,190,000. The average monthly indicated investment and average capitalization for each company formed are given in the following table:

	Monthly	Company
Five months, 1914	$ 7,647,400	$ 497,000
Year, 1915	6,711,100	410,900
Year, 1916	34,978,800	1,748,000
Year, 1917	70,018,283	1,641,053
Year, 1918	35,873,300	524,900
Year, 1919	315,500,500	2,324,128
Year, 1920	232,234,500	1,627,812
Eleven months, 1921	108,185,700	1,355,400

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[1] Received October 1, 1921.

[2] THIS JOURNAL, **10** (1918), 1016.

Chemically Speaking, How's Europe?

By Watson Davis

1418 Rhode Island Ave., Washington, D. C.

We Americans have been hearing much about conditions in Europe since the war. Our friends have gone over, and they have brought us back stories of their impressions of places, things and people here and there. We are interested in knowing how science is recuperating after the years of its serfdom to war; whether it is taking hold again and whether it will succeed in making Europe again worth living in.

This account is a composite picture drawn by three or four scientists who are lucky enough to have been over in Europe this past summer on roving commissions. It is written much as they told it to me and as they would tell it to you if you persuaded them to go over what is now to them an old story. The chemistry of this account often will not stand out pure and unapplied. It will blend into science in general, and in many cases even science will fade into the vivid background of hungry faces, depreciated currency, and war wreckage that is as yet only slightly cleared away.

Conditions in Germany

Scientific Germany is somewhat like a broken man, who has been sick and is now living on his stored vitality of past years. It must not be said that the patient will not recover, but just now scientifically he is largely relying on the achievements of better days before and during the war. There is a tendency to capitalize the things that were developed then.

The dearth of equipment, books, supplies and all the things that make up a workshop for scientists is a real one, not only chemically but in all scientific lines. The talk of poor conditions that we have been hearing is more than mere bluff.

Many of the largest universities and research laboratories, whose names were awe-inspiring in chemical circles before the war, have had practically no American scientific literature since the beginning of the war in 1914. And it is a financial impossibility for them to obtain foreign publications without outside help. The mark has lost so much caste among the moneys of the world that when it gets outside of its own country's borders it can hardly demand anything. Not to know what the chemists of other nations have been doing for seven years is a serious handicap to the work of German scientists. It is declared that in all Germany there is but one set of *The Physical Review*, the journal of the American Physical Society, complete to date. The lack of chemical literature is believed to be just as great.

Universities are having a hard time of it financially. University salaries and grants are notoriously hard to increase in this country, and the conditions are similar in Germany. One of the institutes of the University of Bonn on the Rhine has had a superficially generous increase in yearly funds from the pre-war sum of 17,000 marks to 170,000 marks, but this becomes small indeed when it is learned that it costs 50,000 marks to heat the buildings of the institute.

What the German universities lack in funds and equipment they have a tendency to make up for in students. The research laboratories at Leipsig are declared to be very crowded.

Salaries of professors are meager now in German universities. Before the war many of the university men had independent incomes of their own that supplemented their salaries. For the most part these auxiliary incomes have disappeared. Now nearly every professor has to hunt around for something to do on the side. They have been forced to adapt themselves to do more remunerative things in part of their time so that they may continue to teach.

This situation promises to bring about a more intimate interlacing between the universities and the industries. Those who would normally be doing research in pure chemistry are being forced into commercial research for the industries because of the money there is in it for them.

The glass works at Jena seem to be producing, but it is difficult to tell what was made during the war and what is new production. Quite obviously some was made for war use only.

A journey to a little inn on the top of the neighboring hills revealed a fine 15-cm. telescope with multiple high power eyepieces mounted as though on a man-of-war. Such a fine instrument seemed out of place there. Its only use was to provide magnified peeps at the surrounding country; its only reward was the few coins that went into the penny-in-the-slot device that was attached to it.

Food, which is interesting to the chemist both chemically and physically, is plentiful in Germany, although somewhat restricted as to certain kinds. Milk is the only food that people stand in line for now, and dairy products as a class are difficult to obtain and high in price. If you want white bread and butter you have to pay as much for them as you do for the rest of your breakfast. Vegetables are served liberally, and meat is being used in much the same old German way, largely as sausage and similar products.

Another sign of the times in Berlin is that the pushcart book sellers are offering new and modern books instead of old and second-hand books as they did before the war.

German firms are understood to be planning foreign exploitation of some of the new metals developed shortly before or during the war. One of these is the aluminium alloy that was intended for use as material for dirigible frames. It will be pushed as a material for engines, automobiles, and similar machinery.

Austria

The small area that still remains under the name of Austria appears strangely self-contained. There is seemingly a supply of raw material, and though wages are low there is, or at least was last summer, work for all, and an unemployment problem was not acute.

In Vienna the foreigner can get practically anything he wants in the way of food and other necessities. Although the hotels are hardly up to the standard that was set by them during the tourist trade of pre-war days, they are remarkably good. In the shops of Vienna can be seen many articles from Czechoslovakia, and trade and other relations with the Czechs are rapidly coming back to normal, as far as the exchange permits. Knickknacks from Germany, reminiscent of pre-war days, are displayed. These small importations are indicative of future commercial relations. From a business standpoint there is good feeling among Germans, Austrians, and Czechoslovaks, who just after the war were on very different terms.

Educational Vienna is worse off than the universities of Germany. The University of Vienna has only money enough to heat its buildings one month out of the year, and as a consequence does not heat them at all. Practically the same appropriation for its work is received as before the war, and this is now ridiculously small in purchasing power. One of the institutes receives 5600 crowns a year, which at a certain time last summer amounted to $2.15 in real American money—it is probably worth less now. It would take nearly four years' appropriations for that institute to subscribe to This Journal for only a year. And this was all the money that was available for salaries, heating and equipment, as well as publications. Obviously subscription to foreign scientific periodicals is out of the question. Under these conditions university work there is limited to lectures, given in cold rooms. There is little or no research work.

The effect of low foreign exchange in Europe is brought home by the following incident. A Polish chemist published a paper in the *Journal of the American Chemical Society*. He was asked if he wanted the fifty free separates that each author is entitled to. He did. And innocently he asked for them with covers. In due and routine time he was sent a bill for $1.77, the cost of the covers. He wrote back from Poland: "This is a just bill but just now it would take a quarter of my month's salary to pay it. Can payment be deferred a few years until conditions of exchange are better?" He was told to forget it.

SCIENCE IN RUSSIA

Russia has been a land in the shadow since the Soviet government has been in control. We have heard little about how science has fared in Russia, and that little has been pessimistic.

Now that our relief organizations are penetrating into Russia to ameliorate famine conditions and the Soviet government is sending scientists to the other countries of Europe and to America, we are beginning to get a little information on scientific Russia.

According to a botanist who had been sent into Germany to buy scientific books for the Russian government, the chemists at Moscow are still in their laboratories and, relatively speaking, they have been making out very well. It appears that the Soviets have established a policy of giving the productive academic men, those whose researches can be seen to influence industry directly, the same food and treatment as the children. And the children have been the first concern in Russia, both where the relief missions have and have not reached.

But even with the most liberal treatment in Russia, even though university salaries are paid by the government in part in priceless food rations of the highest grade, the professors have to look around for odd jobs. This is a quotation from a statement made by one of our leading biologists, who has just returned from Russia as a special representative of the American Relief Administration:

> The salaries and food rations of the professors in the University of Kazan had been so meager that not a man was able to live on them, and every professor was meeting his family's needs for food by doing something besides regular university work. The means for keeping himself and family alive were various, but in almost all cases they included the successive sacrificing of personal and household belongings. One professor of biology told me that he made shoes, and that his wife baked cakes and sold them in the city market. He had sold all of his own and his wife's simple jewels and trinkets and one of his two microscopes. Yet this man, who had not been able to see any books or papers published later than 1914, has struggled along with his special researches and has actually achieved two pieces of experimental work on vitamines which seem to me, with my little knowledge of the subject, to contribute certain definite new knowledge concerning these interesting substances.
>
> But beginning in August, there had been a material increase in salary and in food ration. The monthly food ration had been put, in August, on the following basis: dark (mostly rye) flour, 30 lbs.; dried peas, 5 lbs.; cereal grits, 13 lbs.; sweets, (not cane or beet sugar), 2½ lbs.; tobacco, $^3/_4$ lb.; butter, 6 lbs.; meat, 15 lbs.; fish, 5 lbs.; tea, $^1/_4$ lb.; white flour, 5 lbs. The items from dark flour to tobacco, inclusive, had been received, the rest of them promised but not received. About 250 professors and instructors receive this ration. The university buildings are so cold that most of the men do all their work except lecturing in their homes. About 5000 students had registered but only about 10 per cent of them were in actual attendance. The largest departments in point of student enrolment were medicine and science. My friend, the professor of biology, had never before ridden in an automobile until he rode with me in our relief car. About 20 men of the Kazan faculty have died in the last two years.

An impression obtained in Europe is that the Soviet government has been fairly successful in carrying out its program in the territory that it directly controls, that is, within about 300 miles of Moscow. However, as far away from the seat of government as Petrograd, for instance, where control by the central government is difficult, preferential treatment of scientific and academic men has been much more irregular.

Scientific eyes in central Europe are looking longingly toward America. The chemists and other scientists of these states are keen to come to America, where living conditions are ideal in comparison with the situation in their native lands. Many leading American scientists have been flooded with correspondence from those countries and the ultimate object, in most cases, is a place in America. This desire for migration from Europe to America began with the Russian revolution and the exodus of many scientists from Russia.

How an influx of European scientists would affect the conditions of American scientists is problematical. In these times of industrial depression, when many chemists are out of work, it is to be expected that American chemists will be sensitive about the possibility of greater competition for jobs. However, the scientists who wish to come to America because European times are hard will be apt to stay here and in many cases would be valuable additions to science circles in America.

BELGIUM, SWITZERLAND, AND HOLLAND

Belgium is the country that seems to be more nearly back to normal than any other part of Europe. There factories are working nearly in a pre-war fashion and university laboratories are again assuming a peace-time aspect. Belgium, first attacked in the war, has received the first part of Germany's reparations and this has helped to make her the most normal country of Europe.

Switzerland and Holland, the two neutral border states, both face outside competition. They have raised high and stringent tariff barriers to prevent a flood of goods from Germany and Austria and the other low-wage-plane countries from engulfing their own manufacturing establishments. There is a feeling, undoubtedly based on fact, that considerable smuggling is under way and that goods from the outside are appearing for sale in those countries relabeled under native disguise.

The educational situation in Holland is quite similar to that of the rest of Europe. At Leiden the number of students is getting back to normal.

THE CONDITION OF FRANCE AND ENGLAND

France and England are gradually getting back into their old scientific stride.

Paris has been the center for international gatherings since the war and has had the benefit of contacts with visiting scientists of all nations. Industrially the condition of France is nearly as far along as that of her smaller sister, Belgium. Food in France is practically up to normal in quality, although the bread is still not quite what it was before the war.

The University of Paris is suffering from a scarcity of students due to the high living costs. The French of the better class who send their sons to college now find that they can hardly afford it.

In England the university conditions are quite similar to those here in America. The colleges are a little over-full. Industrial depression has forced the young men whose education was interrupted by the war back into college. Industry now has no strong call for them and those who can are entering the colleges to finish their education.

The meeting of the British Association for the Advancement of Science held in Edinburgh this summer had much the tone and spirit of the meetings before the war.

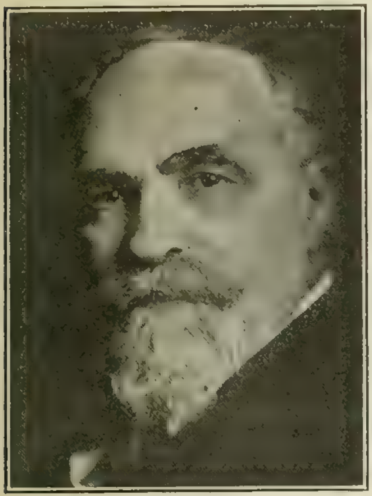
From a food standpoint also, England is getting back to normal. They still have one crude chemical, brown sugar, on their tables, usually along with refined lump sugar, and this seems odd to Americans who find it nearly as hard to buy brown sugar for candy making as they did before the war.

Views of French Chemical Warfare Advisers

Reparations!

That is the answer of Professor Charles Moureu, president of the International Union of Pure and Applied Chemistry, and one of the leading chemists of France, to the question, "What is the most important factor in France's chemical situation?"

"Ten districts devastated. If the Germans cannot pay, well, what can we do?" Uppermost in the minds of Frenchmen is this question of the German indemnity. Germany must pay. Germany by her reparations must reëstablish a large part of France, not alone chemically, but industrially. This is without a doubt one of the all-enveloping thoughts in the minds of the French delegates now in Washington at the Limitation of Armaments Conference. Professor Moureu is attached to the French delegation as official adviser on chemical warfare.



Harris & Ewing

Professor Charles Moureu

Professor Moureu is professor of organic chemistry at the Collège de France and he has been a leading figure in chemical research of that country. Some of his latest work has been on the origin of helium.

Professor Moureu is enthusiastic over the future of the International Union of Pure and Applied Chemistry.

Next year when the meeting is held at Lyons, France, in June, he believes that twenty-five nations will be represented at this gathering of the chemists of all nations. At the Brussels meeting held this summer twenty-one nations sent representatives.

Harris & Ewing

Professor André Mayer

Professor Mayer is now professor at the Université de Strassbourg in repatriated Alsace. He established the tuberculosis laboratory at the Puteaux near Paris which during the war became the laboratory of the American Chemical Warfare Service.

"Will Germany be included?"

Emphatically no. Germany, the country that will not pay the indemnity, Germany, the country that devastated France, that Germany cannot be allowed to join the international organization of chemists. This Professor Moureu strongly believes; this seems to be the opinion of most of France, scientific and nonscientific. They are not ready now to fraternize with recent enemies; they are not even ready to meet them scientifically.

Professor Moureu tells how ten committees of the International Union are at work.

"Two are headed by your countrymen," he said. "Prof. F. W. Clarke, of your Geological Survey, is honorary chairman of the committee on chemical elements, which has sub-committees on radioactivity, isotopes, and atomic weights. Your great Professor Richards of Harvard is the chairman of the committee on nomenclature."

But while industrial France, including the chemical industries, is slowed up by German slowness of paying, scientific France is organized.

France's seven chemical societies are affiliated and combined into a federation of chemical societies. Similarly all the biological societies of France are brought together, and also all the physical societies are federated. Those organizations dealing with the law, philosophy and history also come within the category of science, and are all brought together in one federation. These four federations have been fused, and there has emerged the Conféderation de Sociétés Scientifiques, corresponding in a way to our American Association for the Advancement of Science.

Then also there is the National Committee of Research, with four councils of chemistry, physics, biology, and mathematics. This organization is official and is supported by the government. It is similar to our National Research Council and is affiliated with the International Research Council.

The future of chemical warfare is interesting to chemists of America, France, and the rest of the world. Perhaps the Limitation of Armaments Conference will have something to say about it. Professors Moureu and Mayer are here to advise M. Viviani and France's other representatives on the chemical warfare that was inaugurated in their country by the Germans. But no, they are here officially. They cannot talk about chemical warfare. I must hardly mention it. So I have not.

A Lesson from History—Lest We Forget

By Charles E. Munroe

National Research Council, Washington, D. C.

The admirable address by Dr. Haller on the "French Chemical Industry during the War"[1] and "La chimie et la guerre" by Dr. Charles Moureu in Masson et Cie's series of "Les leçons de la guerre" present most vivid pictures of the almost superhuman efforts by which the enormous and varied demands for war supplies were met; the many ingenious devices by which the splendid organizations created increased the speed of production and effected economies in operation; and the resourcefulness shown in adapting such material as could in any way be obtained to the many and various needs. They record the wonderful achievements of a most brilliant epoch in the application of chemistry to supplying the bitter needs of a nation in great distress. But it is repeatedly emphasized throughout these histories that in 1914 France was, as regards the supplying of its needs for chemical products, a very dependent nation.

Yet recalling that the use of picric acid as a fragmentation charge for high explosive shell was developed to complete operativeness by Turpin in France soon after 1885, and that the many other nations which adopted this material as charges for H. E. shell, under the names of Lyddite, shimose and other pseudonyms, patterned their practice on his, it is astonishing to learn that in 1914, notwithstanding that there were then in France a large number of accomplished and most competent chemists and chemical engineers, the supplies of phenol for the manufacture of the picric acid which had been adopted by the French government for its H. E. shell, "came from foreign countries and particularly from Germany."

This is the more remarkable when it is recalled that France had previously passed through severe trials and been succored by its chemists, as at the time of the French Revolution when it was sorely beset by enemies without and within. So strenuous were conditions that the *Annales de Chimie* was forced to suspend publication, but when in 1797 the tide of struggle turned and victory was wrested from the enemy by the armies of France, publication was resumed with Volume 19, which carries the following preface:[2]

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[1] *Bull. Soc. d'encour. l'ind. nat.*, **132** (1920), 761.

> The *Annales de chimie* has been suspended during three years following the publication of volume eighteen. The necessity for each devoting oneself solely to the defense of the Republic; the events of the revolution; and finally the public occupations and functions of its authors have naturally compelled this suspension. But the time has not been entirely lost to science; chemistry, above all, has been cultivated with an activity and success to which all testify; she has developed for the defense of the country truly unexpected resources and expedients. Her ability to relieve immediately the most urgent needs has rendered her most precious and commendable in the eyes of the lovers of mankind, and of all true citizens. Further the number of those becoming students has increased each day; it has become a fundamental topic in all modern schools, and above all in those which seek the higher planes of human knowledge.
>
> Among all the civilized nations, where one works without ceasing for the perfection of reason, the sciences which influence territorial and industrial production, and among which chemistry to-day occupies the first rank, are held in general esteem. The cultivation of the fields, the multiplication of animals, the establishment of manufacturers, the exchange of the industrial creations for the products of other people constitute the true source of the prosperity of nations to which all men are called according to their abilities and where they find, in serving their country, their chief pleasure.
>
> Chemistry clarifies the practice of the arts; without her neither constancy in products, economy in process, nor perfection in operation can be hoped for. Unable to know in advance and to calculate the results, manufacturers have often made errors which have lost them their establishments. Consequently many chemists have in recent years become manufacturers and already France has ceased to be tributary to other nations for a great number of useful products; the preparation of the mineral acids, different salts, metallic oxides, dyes, and glass, multiplied in France during the last five years, are authentic proof of the inestimable advantages of chemistry. Without the light of this science from where would have come the quantities of saltpeter and powder for our armies which was made in the last four years? From where the copper, iron, steel, potash, soda, leather, and all the other precious materials which have enabled us to conquer our enemies and to maintain our existence? Without chemistry we would have been helpless.
>
> At the moment when victory has crowned our efforts, when talent has been recognized and called to the service of the State; at the moment, above all, when new schools have been opened in the Departments which seek to spread knowledge and make known its needs, the authors of the *Annales de chimie* believe it a pressing duty to go on again with the circulation of this journal. Their aim is to carry the torch of science into all workshops; to make known the new processes; to describe the little known or unused arts; to improve bad practices; to correct errors which occur too often in many of our factories; to describe means for the utilization of neglected or wasted by-products; to expose the often misleading trade secrets and the perfidious charlatanism; to establish lucid theories of the most obscure operations; to direct the nearly always unassured or uncertain steps of the manufacturer; to destroy mystery, and to repress fraud. In a word, to serve science in the most exact manner and to increase the varieties of national industry.
>
> We believe that, without neglecting chemical philosophy, it is its special applications to the useful arts that will clarify and improve those arts. Brilliant and ingenious theories will not be refused, particularly if they have useful applications. It is for intelligent and reliable artists, manufacturers, workmen, and merchants that this work is especially designed. At the same time savants and philosophers will find records of the progress of physics and the march of human events. It is fine to be able to view the improvement in the arts and also in well doing among a great people.
>
> It is hardly necessary to say that all possible effort will be made to join to the discoveries made in France those made by other nations where chemistry and the chemical arts are cultivated with success, and especially Germany, Spain, Holland, Italy, and England.
>
> The authors of the *Annales de chimie* having undertaken to continue their work propose to present in the nineteenth and twentieth volumes the principal discoveries and most remarkable achievements in chemistry made in France between September 1795 and January 1797.

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[2] *Ann. chim.*, **19** (1797), 5.

SOCIAL INDUSTRIAL RELATIONS

Waste in Industry

By H. W. Jordan

Syracuse, N. Y.

The report upon the research made this year by the Federated American Engineering Societies, under leadership of Herbert Hoover, is issued as the book "Waste in Industry," published by the Societies.[1] The research marks a new phase of engineering in that the creators of modern industry, the engineers, have applied their methods of investigation by research and mathematical analysis to industrial management and industrial contact with the public.

This research upon six typical branches of industry, building, men's clothing, shoe manufacturing, printing, metal trades and textile manufacturing, disclosed that on the average labor is responsible for 16 per cent of the waste, defective relations with the public for 16 per cent, and management answerable for 68 per cent.

THESE SUMMARY FIGURES ARE BASED ON THE FOUR MAIN CAUSES OF WASTE:

1—Low production caused by faulty management of materials, plant, equipment, and men.

2—Interrupted production, caused by idle men, idle materials, idle plants, idle equipment.

3—Restricted production intentionally caused by owners, management, or labor.

4—Lost production caused by ill health, physical defects, and industrial accidents.

As Mr. Hoover says in the foreword of the book, "We have probably the highest ingenuity and efficiency in the operation of our industries of any nation. Yet our industrial machine is far from perfect. The wastes of unemployment during depressions; from speculation and overproduction in booms; from labor-turnover; from labor conflicts; from intermittent failure of transportation of supplies of fuel and power; from excessive seasonal operation; from lack of standardization; from loss in our processes and materials—all combine to represent a huge deduction from the goods and services that we might all enjoy if we could do a better job of it."

THE SURVEY SHOWS SUCH STRIKING SIMILARITY BETWEEN THE SIX INDUSTRIES that it indicates the existence of universal laws that govern industrial mass action. Although equipment of the several industries varies widely, five of the six showed close approximation to the above average distribution of waste. Textile manufacture, the oldest American industry, showed but 50 per cent of its waste due to management. Its greater losses, 40 per cent, are due to outside contacts.

Interrupted production caused by seasonal conditions, competitive trade practices, and unbalanced operations between departments of manufacturing plants were a large cause of waste. Interruption due to labor strikes was found less serious than is popularly supposed, because so many strikes are in seasonal trades, like manufacture of clothing or the building trade, where the loss is not absolute because it is made up by energetic work at a later date.

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[1] "Waste in Industry," McGraw-Hill Book Co., Inc., New York, N. Y., 1921. xi + 409 pages. Price, $4.00.

Destructive competition, absence of coöperation, lack of comparative statistics of industry coöperatively collected and intelligently used are among principal causes of waste. Lack of standardization of machines and of methods, maintenance of an excessive number of patterns, sizes, and styles, and extreme excess equipment contribute heavily to waste.

THERE ARE APPROXIMATELY 6000 BRANDS OF PAPER, 50 per cent of which are more or less inactive. Duplication of brand serves no useful purpose and ties up money in unnecessary stock. As an example of the disregard of standard size, the Federal Reserve Bank check will not cut without waste from any regular paper sizes. A draft questionnaire issued during the war was of such nonstandard size as to require special filing cabinets. The Technical Publishers' Association on measuring 927 catalogs found 147 different sizes. A trim of one-quarter inch on a 6 × 9 page is equal to 7 per cent of the total cost of the paper. Among current magazines there are 18 variations in width and 76 in length of page or column. Among trade paper publications there are 33 variations in width and 64 in length. Among newspapers there are 16 in width and 55 in length. These variations cost the public not less than a hundred million dollars each year. Standardization of newspaper columns to one size would make possible an annual saving of $3,000,000 to $5,000,000 on composition and plates alone.

* * *

LACK OF EFFECTIVE PLANNING AND ADMINISTRATION in one large typical plant wastes one-fifth of the worker's time. A shoe factory having a capacity of 2400 pairs of shoes a day could turn out for a considerable period only 1900 pairs because of shortage of needed racks. Another factory had 50,000 pairs of shoes tied up in the fitting room instead of the normal 15,000 because of congestion of operations. In another case a factory producing 700 pairs of shoes a day had 36,000 pairs in its fitting room, or ten times the normal supply. An entire factory was held up for several days waiting for leather heels. From shop records it is found that the average loss in clothing factories during running time, not including shut down, is between 30 and 35 per cent. If we call 80 per cent running time the maximum readily attainable, this means a possible increase of nearly 20 per cent in productive capacity, and a similar increase in plant capacity.

* * *

Since most strikes occur in seasonable employments, it can be deduced that output is not necessarily penalized, for it is often possible to make up the losses incurred by strikes through increased production at other times. More coal was mined in 1910 than in 1911, although the former year witnessed many protracted strikes involving large numbers of employees. The year 1912, with 47 per cent of the entire labor force out on strike and with an average loss per man of 40 days, showed an increased output of coal per man, per day and per year, and six days more employment than in 1911, which was relatively strikeless.

* * *

Clothing factories are built 45 per cent larger than is necessary; printing establishments are from 50 per cent to 150 per cent overequipped; the shoe industry has a capacity of 1,750,000 pairs of shoes a day, and produces little more than half that number; throughout the metal trades, standardization of products would permit of large reductions in plant and equipment.

* * *

Practically all industries are seasonal. The clothing worker is idle about 31 per cent of the year; the average shoemaker spends only 65 per cent of his time at work; the building trade workman is employed only about 190 days in the year or approximately 63 per cent of his time; the textile industry has regular intervals of slack time; during the past 30 years bituminous coal miners were idle an average of 93 possible working days per year.

* * *

ABSURD LABOR UNION REGULATIONS CAUSE WASTE. As carpenters' helpers are prohibited from using carpenters' tools, carpenters are required to do such work as stripping forms from concrete, work that helpers could do more cheaply and as well. Hoisting engineers claim the right to run all types of engines, including automatic, gas driven pumps. On one job a contractor had to hire a union engineer at $8.00 per day simply to start a pump in the morning, oil it occasionally, and stop it at night.

* * *

THE PUBLIC IS RESPONSIBLE FOR ABOUT ONE-TENTH OF THE WASTE DISCLOSED. Excessive numbers of styles, combative rather than coöperative public opinion, and crowding manufacture and trade into short seasons by failing to standardize wearing apparel are among industrial sins of waste of which the public is guilty.

These citations from the report are sufficient to show its thoroughness and to bring to notice elements of waste that are plainly preventable.

UNDERLYING THE STUDY ARE FOUR FUNDAMENTAL PRINCIPLES THAT MERIT our serious attention. First, that humanity, whether management, labor or public, proceeds along the same ways in each industry in strict, readily discernible accordance with laws that are world-wide;

THAT PROFITABLE PRODUCTION AND SUPERIOR EFFICIENCY RESULT FROM COÖPERATION; while loss, interruption of industry, and discontent among employees and public spring from absence of coöperation;

THAT ACTION AND REACTION ARE EQUAL IN HUMAN INDUSTRIAL RELATIONS as they are in mechanics; and that the Golden Rule, which is one wording of the law of equal action and reaction, is not a mere soothing expression of a pleasing ethical theory, but that it is a primary law of self-preservation in industry, commerce, and all human relations;

AND FOURTH, THAT RESEARCH, by the methods of applied science and mathematical analysis which engineers and chemists have applied to machines and processes, is equally applicable to every phase of industry, commerce, and human affairs.

A main value of the Federated Engineers' study of waste in industry is this proof that all human relations are capable of interpretation and improvement by scientific research. "The future of civilization depends upon the widening spread and deepening hold of the scientific habit of mind," says John Dewey. Continuance of profitable industry in its readjustment to the conditions arising from the World War depends upon scientific research that will extend into all human relations of industry as deeply and thoroughly as it has delved into the applied sciences that yielded the automobile, moving pictures, aviation, by-product coke and contact sulfuric acid—industries of applied science that did not exist a half century ago. As the report says:

> While certain industries are ahead of the rest in plant research, the need for more intensive research activity is apparent in every industry. One industry which is backward in this respect is clothing. In the majority of men's clothing plants nothing approximating research is practiced to improve materials, processes, equipment, or product. The assertion probably will not be challenged that there is not a single individual throughout the entire industry who is solely engaged in research and is thus without operating duties. In the shoe industry there is lack of information as to market demands in this country and abroad. In all leather industries there is need for scientific research to aid in predicting the kinds and quantities of leather required.

INDUSTRIAL MANAGEMENT HAS PAID TOO LITTLE ATTENTION to waste and loss of profit arising from disregard of social industrial relations with employees and the public. Failure to realize that these human relations are responsive to scientific research has resulted in a large by-product of industrial ill will, ill will not only of employee but of the public; ill will reflected in types of taxation and government regulation as senseless and costly as the $8.00 engineer who starts and stops an automatic pump. Here, too, we find reaction equal to action.

THE REAL TEST OF INDUSTRIAL CONSOLIDATION IS TO COME IN THE NEXT TWENTY YEARS. The Federated Engineers say "There is probably direct connection between the increase in size of industrial plants, and the statement made by Bradstreet to the effect that, while 'incompetence' had always bulked large as a cause of business failures, by 1912 it had grown to be the chief cause and by 1919, 38.2 per cent of all failures were caused by it. During this period plants were rapidly increasing in size because of the growth of the country, and a higher standard of management was at the same time being required."

In my opinion the next phase of corporate industry will be reversion to its original units, operated by local, resident management in social harmony with their several communities; with present absentee management supplanted by coöperative management acting in close accord with mathematical or statistical information secured by research like that of the Federated Engineers.

"Underlying the balance sheet, the Ethical Factor—expression of fairness in all relations—must be distinctly plus, not minus, or any industry cannot survive," says Babson. Future industrial coöperative management will be characterized by extension of practical coöperation to employees and to the public, with proportionate elimination of the vast fund of antagonism and industrial ill will toward employers as a class.

THIS RESEARCH UPON WASTE IN INDUSTRY IS AN EARLY PROOF OF THE NEED OF SUCH COÖPERATION. Equally convincing proof is the widespread abandonment of humanitarian work by corporate management since the war, and the dropping of a large portion of scientific industrial research as well.

HUGE CORPORATE INDUSTRY HAS ENTERED THE THIRD GENERATION OF THOSE WHO FOUNDED ITS COMPONENT UNITS. They say in Japan—"The third generation makes or breaks a dynasty." As Lothrop Stoddard expresses it: "The melancholy trinity—David, Solomon, Rehoboam—has reappeared with depressing regularity throughout history." In American corporate industry we are witnessing, and enduring, the third generation stage. The ultimate result will return to more individualistic, local, resident management, under a national, coöperative rather than competitive system.

It is a principle of human progress that it works in circles; that inventions or great social movements begin in simple, rudimentary forms, advance through extreme complication and, in their ultimate perfection, come back to the simple, essential elements from which they started. Thus the steam engine was first Hero's revolving cups, and next the reciprocating engine of Watt. In the modern turbine engine it has returned to Hero's principle.

THIS SURVEY OF WASTE IN INDUSTRY IS AN INVALUABLE SERVICE TO COMMUNITY, STATE, AND NATION. It points the way to the return of our industries to their ultimate, yet original, form of single plant units, efficiently managed and harmoniously conducted by men and women who make each industry their life career in the city or town they adopt as their home. By that return to first principles we shall regain the immensely valuable social force of American individualism, strengthened by a system of nation-wide, coöperative industrial relations based upon laws which govern world-wide human relations; laws that chemists and engineers will reveal and apply by scientific industrial research. Thus we shall attain industrial, social, world-wide peace, with enduring prosperity through elimination of industrial and social waste.

NOTES AND CORRESPONDENCE

Liability for Laboratory Accidents

Editor of the Journal of Industrial and Engineering Chemistry:

The Court decision which awarded a Cornell woman student $25,000 damages because of alleged negligence on the part of the College Department of Chemistry, by which she lost the sight of one of her eyes, as reported in the November 1921 issue of THIS JOURNAL, certainly gives those of us who teach beginners food for serious thought. The outcome of the appeal to the highest court will be awaited with great interest.

I have long opposed the usual method of dispensing chemicals in laboratories where beginners in the subject are at work, namely, letting the student help himself from bottles on a side shelf or table. I have seen so much trouble, and so many accidents, result from this method that I long ago discarded it as dangerous and inefficient, and have substituted a "dispensing stockroom," where the responsibility for giving out the correct chemicals, and in right amounts, is upon the stock clerk. There are so many chances that a student will meet with accident, even with the proper chemicals, that we should strive to eliminate entirely the many chances of accident due to getting the wrong chemicals.

I have never yet seen chemicals left out within reach of students that were not contaminated, one by the other, and while the testimony of Professor Chamot states that no lime was found in the unused remainder of the mixture made for the experiment, and the case under consideration seems to be clearly one of carelessness on the part of the student, there is always the possibility of accident due to the presence of a chemical in a bottle labeled as containing some other.

A case in point, which happily did not end in disaster, occurred in my own laboratory when a stock clerk, too lazy to do as he had been told, let the students help themselves. The students had been pouring potassium chlorate from a wide-mouthed container into a test tube. This procedure naturally resulted in the spilling of much of the substance on to the table. Students are notoriously prone to leave bottles unstoppered, and on this occasion a bottle of powdered sulfur was receiving a very liberal addition of the chlorate. Prompt removal of this contaminated material is probably all that saved some one from a bad explosion. That particular stock clerk was eliminated from the staff.

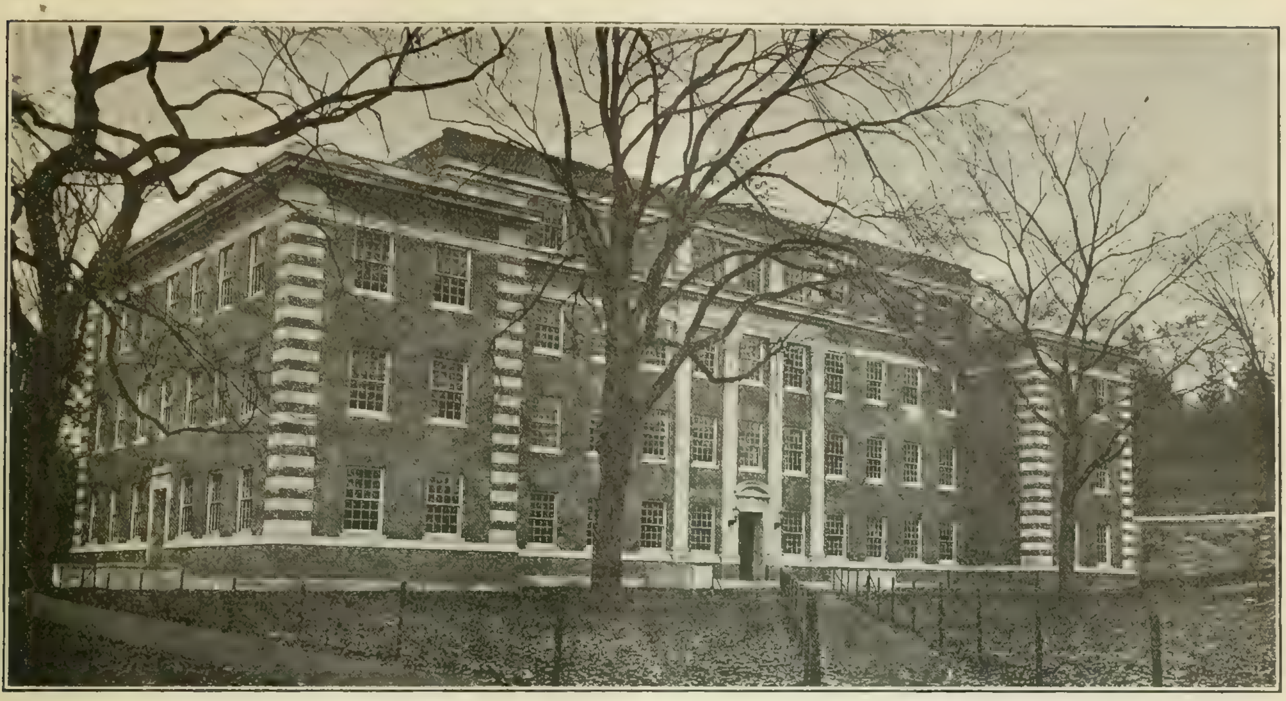
Contamination of fine chemicals by interchange of stoppers is also a frequent occurrence in a beginners' laboratory. This is especially true of solutions. I have had a class lose the work of nearly a whole laboratory period because a stock clerk (the same one, by the way) had let some student mix up stoppers on two bottles, one of which had contained a chemically pure substance in solution.

With free access to chemicals, foolhardy students will "try anything once." I have, when a student myself, seen another student take the opportunity, when the teacher had left the laboratory temporarily, to pour some material from nearly every bottle on the shelf into a beaker just to see what would happen. You may say that is the research spirit manifesting itself early, but I shudder to think that he might have produced hydrocyanic acid had he picked out *all* the bottles on that shelf. A kind Providence probably saved us all that day. The teacher wisely removed the potassium cyanide after hearing of this escapade.

If the ruling by the Court, that it is the duty of the Department of Chemistry to analyze all chemicals received from manufacturers before they are dispensed to students, is upheld by the higher Courts, colleges will feel required to make these analyses. This will add considerably to the expenses of instruction, and if the chemicals are bought in small containers the additional expense will be very large.

If the further ruling is upheld that it is the duty of the Department to ascertain by chemical examination whether the contents of all bottles in the student laboratories are in exact accord with their labels, a continuous run of analyses would have to be made on *all the bottles all the time* the students are present. This would seem to preclude the use of the system of dispensing where the students have access to the bottles, (for students are bound to contaminate the chemicals); otherwise the college must assume the liability incurred in neglecting to make such continuous analyses.

The case of the male student whose explosion was due to the fact that he had scraped up some white chemical that had been



Steele Chemistry Building, Dartmouth College

This new laboratory which was dedicated October 29, 1921, was in part the gift of the late Sanford H. Steele, formerly president of the General Chemical Co. At the dedication, Dr. Henry P. Talbot delivered an address on "Fifty Years of Chemistry: Our Heritage and Our Obligations"

spilled on the table, and which was evidently not "lime" which the experiment required, seems to me to be argument enough to persuade any teacher who has to supervise a beginners' laboratory that it is not wise to let these inexperienced students help themselves. Some students are always slovenly in pouring out chemicals and seem to care little how much they spill. It always seems to me that one slovenly student contaminates the others in the laboratory. They see that he "gets by" (as they say) without cleaning up what he has spilled, and they try to do likewise. This, if true, is another good argument for a controlled stockroom

At Brown our "dispensing stockroom" opens directly into the laboratory, and a student assistant deals out the chemicals asked for by the students. Only dilute acids and ammonia are on the benches, and these are the only chemicals, outside of water, to which the students may help themselves. We are thinking seriously of eliminating all but the water.

While this system is not infallible, it is easier to find the source of trouble, and to place the responsibility for it.

Regrettable as it is that the Cornell student lost the sight in one eye, for which loss money alone can hardly be a recompense, it does not seem clear to me that the college should be held liable for the financial recompense in this case, which appears so clearly one of neglect on the part of the student.

If the higher courts sustain this verdict there seems to be nothing left for the colleges to do but to take out liability insurance to cover such cases. It is certain they cannot afford to make the analyses.

H. F. Davison

Brown University
Providence, R. I.
November 14, 1921

Another Case of Spontaneous Combustion[1]

Editor of the Journal of Industrial and Engineering Chemistry:

At about 2:30 P. M. on July 15, 1921, a volume of white smoke was discovered arising from the top of a tank installed in the yard of the Experimental Kelp Potash Plant of the U. S. Department of Agriculture at Summerland, California. The tank being of wood, the impression created was that the tank itself was on fire, but it was immediately discovered that a cotton sack lying on top of the tank was burning vigorously and that this was giving rise to the smoke.

This sack, it developed—an ordinary white cotton flour sack—had been used in the filtration of crude sodium chlorate employed as a reagent in the manufacture of iodine from kelp potash brines, and when the iodine plant had been shut down two months previously, the sack had been thrown on top of the tank where it had remained ever since. Since the iodine plant was constructed out-of-doors, without a protecting roof, the top of the tank and the sack lying on it were exposed to the sun's rays, and it was so situated as to be exposed to the sun all the morning. The day in point was a brilliantly clear one, though not unusually warm.

The top of the tank is about 7 ft. from the floor, which fact would discount the idea that the fire could have had its origin in the carelessness of smokers. Furthermore, inasmuch as the plant was shut down and in a stand-by condition, no one entered it but the guards. The chances of the fire originating other than spontaneously, accordingly, seem negligible.

On the other hand, the facts that the sack in question was impregnated with sodium chlorate; that it was a second-hand flour sack and possibly had not been entirely freed from flour; that it accordingly was highly inflammable; that the sun's rays in this locality are highly actinic, all combine to substantiate the conclusion that the fire was another case of spontaneous combustion. It is believed that the reaction was started through the influence of the chemically active rather than the heat rays of the sun.

The phenomenon was witnessed by Mr. P. S. Shoaff, the superintendent, and Mr. H. G. Tanner, chief chemist, who concur in the above conclusion.

J. W. Turrentine

Experimental Kelp Potash Plant
U. S. Department of Agriculture
Summerland, California
September 14, 1921

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[1] Published with permission of Secretary of Agriculture.

Determination of Salt in Petroleum

Editor of the Journal of Industrial and Engineering Chemistry:

In the paper on the subject of "Determination of Chloride in Petroleum," by Ralph R. Mathews[1] I have noted with interest his scheme of separating salt water by mixing acetone and water with the oil under examination.

In this laboratory we have for several years been estimating salt after burning off an oil. For rapid control we weigh from 10 to 20 g. of a fuel oil in a dry nickel dish of about 250-cc. capacity, and heat the dish and contents over a Bunsen gas flame. When the oil is fuming thickly, the gases over the dish are ignited with the Bunsen flame, and the heating is continued until the oil fumes burn out. The Bunsen flame is withdrawn for a minute, 75 cc. of water are added, and the mixture is boiled vigorously for a few minutes. The dish is cooled in a vessel of cold water until cool enough to handle, and the contents are filtered and washed several times with water, scrubbing out the dish. After the addition of a few drops of 1:10 potassium chromate solution, the filtrate and washings are titrated as usual with standard silver nitrate, and the results are calculated to NaCl.

There is left in the dish a mass of charred matter which, after sufficient washing, does not retain more than traces of salt, and need not be completely removed from the dish before another determination is made. The dish does not get to a red heat while the oil is burning off, and the charred mass provides a means of protecting NaCl from volatilizing. The nickel dish is not used for any other work.

If the oil contains an abnormal quantity of salt, it foams and spatters badly, and a lower flame is used for the first part of the heating operation.

Our specification on fuel oil for use in open hearth and forge furnaces does not permit the presence of more than 0.25 per cent of salt. However, it is only rarely that we have met with samples of oil running as high as 0.10 per cent. On the other hand, in composite samples from bunches of ten carloads we have never found a total absence of salt.

George T. Dougherty

American Steel Foundries
Chicago, Illinois
April 20, 1921

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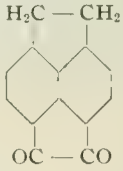
[1] This Journal, **13** (1921), 325.

The Chemistry of Acenaphthene and Its Derivatives

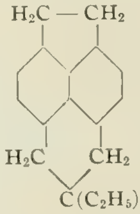
Editor of the Journal of Industrial and Engineering Chemistry:

The excellent summary of the chemistry of acenaphthene and its derivatives by D. A. Hahn and H. E. Holmes which appeared in the September number of This Journal[1] undoubtedly will serve the purpose for which it was written and stimulate investigation in this interesting field. As, however, this paper was received on June 20, 1921, and it is stated that the synopsis represents all the references to the chemistry of acenaphthene and its derivatives which could be obtained from a fairly close search of the literature, new workers in this field may possibly overlook the most recent work. It appears of interest, therefore, to bring this subject up to date by the addition of a short note.

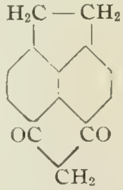
A. Zinke and E. Raith,[2] F. Mayer and W. Kaufmann,[3] F. M. Rowe and J. S. H. Davies,[4] K. Fleischer and P. Wolff,[5] and K. Fleischer, H. Hittel and P. Wolff[6] have described new derivatives of acenaphthene and, in some instances, have revised the melting points of derivatives previously known. New derivatives include pyridino-4,5-acenaphthene, melting at 67°[2] or 60° to 61°,[3] obtained by the action of concentrated sulfuric acid, glycerol and nitrobenzene on 5-aminoacenaphthene; tetrabromoacenaphthene, melting at 180° to 181°;[3] 5-ethylacenaphthene, boiling at 160°/20 mm.[3] or melting at 42.5° to 43°,[5] which forms a picrate, melting at 95° to 96°,[3] and is oxidized through 4-ethylnaphthalene-1, 8-dicarboxylic anhydride, melting at 180°,[3] to naphthalene-1,4,8-tricarboxylic acid; 5-nitroacenaphthenequinone, melting at 199°[3] or 218°,[4] forms a monophenylhydrazone, melting at 186°[3] or 234° to 235°,[4] and a diphenylhydrazone, melting at 148°, and is converted into the corresponding nitronaphthaldehydic acid, melting at 245° to 247°, by the action of concentrated potassium hydroxide; 5,6-dinitroacenaphthenequinone, melting above 300° with decomposition,[3,4] forms a monophenylhydrazone, melting at 287°; a diacetylacenaphthene, melting at 146°;[5] 5-acetylacenaphthene readily condenses with benzaldehyde to form crystalline benzylidene derivatives, the *o*-chlorobenzylidene compound melting at 113°;[5] 6-acetyl-5-ethylacenaphthene, melting at 110.5°;[5] 5,6-diethylacenaphthene, melting at 10° to 11° and boiling at 182°/14 mm.;[5] pyracenehemiquinone



melting at 226°,[5] obtained by the action of oxalyl bromide on acenaphthene in the presence of aluminium chloride; 5-bromoacetyl-acenaphthene, melting at 180°;[5] 2,2′-diethylperiacenaphthindane

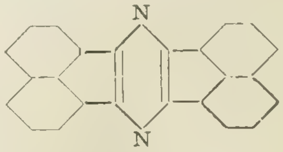


melting at 93° to 95°,[4] obtained by the reduction of 2,2′-diethylperiacenaphthindane-1 :3-dione; periacenaphthindanedione



melting above 300°.[6]

The substance regarded by Graebe[7] as acenaphthenequinoneimide has been shown by A. Schonberg and F. Nedzati[8] to be acenaphthylene-1,2-azine



Instances in which melting points have been revised are 5-aminoacenaphthene, melting at 104° to 105°;[4] 5-acetylaminoacenaphthene, melting at 238°,[4] for 192° given by Sachs and Mosebach;[9] 4-nitro-5-acetylaminoacenaphthene, melting at 255°[4]

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[1] This Journal, **13** (1921), 822.

[2] *Monatsh.*, **40** (1919), 271.

[3] *Ber.*, **53** (1920), 289.

[4] *J. Chem. Soc.*, **117** (1920), 1344.

[5] *Ber.*, **53** (1920), 925.

[6] *Ibid.*, **53** (1920), 1847.

[7] *Ann.*, **276** (1893), 9.

[8] *Ber.*, **54** (1921), 238.

[9] *Ibid.*, **44** (1911), 2860.

for 253°;[9] 4-nitro-5-aminoacenaphthene, melting at 222°;[4] 4-nitronaphthalene-1,8-dicarboxylic anhydride, melting at 229° to 230°[4] for 220° given by Graebe.[10]

In conclusion it may be pointed out that the reason why the literature contains such a variety of melting points for certain derivatives of acenaphthene is that, in some instances, very numerous recrystallizations are required before a constant melting point is obtained, although the product may melt quite sharply after each crystallization.

FREDERICK M. ROWE

DYESTUFFS RESEARCH LABORATORY
COLLEGE OF TECHNOLOGY
MANCHESTER, ENGLAND
September 19, 1921

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[10] *Ann.*, **327** (1903), 77.

The Determination of Metallic Aluminium and Aluminium Oxide in Commercial Metal

Editor of the Journal of Industrial and Engineering Chemistry:

The paper of the above title in the September number of THIS JOURNAL warrants comment as to fundamental premises, logical development, and conclusions.

The density of hydrogen is assumed in the paper to be 0.08994, whereas the universally accepted value after Morley is 0.08987.

Apparently the weight of aluminium used was not reduced to the "*in vacuo*" basis. Adequate evidence is not adduced to indicate the purity of the hydrogen gas evolved in the reaction. However, it is in that portion of the paper headed "Data" that the logical development of the author's idea may be seriously questioned.

Column 1, Table I, shows the results obtained when it is assumed that 1 g. of "100 per cent pure" aluminium will displace 1.24068 liters of hydrogen (27.1 being the atomic weight of aluminium). The results obtained are quite at variance with what the author expected. Another chemist by other methods had determined the aluminium content to be 98.60 per cent. The author of the paper under discussion proceeds to accept these results of the other chemist and seeks to make his own results conform to them. Since the author finds 99.64 per cent, he assumes that the hydrogen equivalent (1241) employed by himself must be in error. He then solves the following proportion for X (the number of cc. of H equivalent to 1 g. aluminium):

$$X:1241 = 99.64:98.60$$
$$X = 1254.1$$

Now since a new value for the hydrogen equivalent of aluminium is obtained which confirms the other chemist's analysis, it is stated that a new atomic weight of 26.81 is indicated for aluminium. However, there is a failure to state that the value of 98.60 per cent found by the other chemist depends upon the atomic weight of aluminium being 27.1. If this chemist had used 26.81 as the atomic weight of aluminium instead of 27.1, he would have reported 98.36 per cent as the metallic aluminium content of the sample in place of 98.60 per cent actually reported. This in turn would lead the author of the paper under discussion into further difficulties, and he must perforce adopt still another value for the atomic weight of aluminium.

The author's statement that 1 g. of aluminium will displace 1254.1 cc. of hydrogen by reaction with a suitable reagent implies an atomic weight of 26.81 for aluminium. Since the author used as a basis of his calculation an analysis depending upon the atomic weight of aluminium being 27.1, we are forced to the conclusion that the proposed value of 26.81 is somewhat doubtful, depending as it does on the assumption that the atomic weight is 27.1.

The author has adduced no evidence to the effect that the accepted value for the atomic weight of aluminium is in error. Consequently, since the accuracy of his method, *i. e.*, the conformity of his results to those obtained by Rhodin, hinges on 26.81 being the atomic weight of aluminium, we are forced inevitably to the conclusion that the proposed method is unsound or that Rhodin's analysis is incorrect, or that both are in error.

As a matter of interest it may be pointed out that if the author's data for Run 106 are recalculated on the assumptions that the density of hydrogen is 0.08987, that the atomic weight after Richards and Krepelka is 26.963, and that the sample weight should be reduced to "*in vacuo*," we find a metallic aluminium content of 99.05 per cent. Again, if we summate Rhodin's analytical results for impurities other than Al_2O_3 we find them to total 0.95, which gives metallic aluminium content by difference of 99.05 per cent.

The author has not established the fact that oxide in metal is a serious problem, and no serious student of chemistry can agree with his conclusion that he has devised a method for the accurate estimation of metallic aluminium (and of oxide, indirectly) in commercial aluminium.

H. V. CHURCHILL

ALUMINUM COMPANY OF AMERICA
PITTSBURGH, PA.
September 20, 1921

. . . .

Editor of the Journal of Industrial and Engineering Chemistry:

The author frankly admits that in the paper under discussion he has inadvertently used what is probably a less accurate value of the weight of a liter of hydrogen than that of Morley, that no correction was made of weighing to the "*in vacuo*" basis, and that he failed to note the contradiction involved in his calculation of a new atomic weight of aluminium from data based on the present accepted value of 27.1.

He thanks Mr. Churchill for calling his attention to these matters and has corrected his data to conform to the suggested changes. After correcting weighings to "*in vacuo*" basis, using 0.8987 as the weight of a liter of H_2 and 27.1 as the atomic weight of Al, he obtains the figures shown in Column A below, which are placed along with Column I of the table as it appeared in the paper in question.

RUN	I	A
106	99.64	99.55
108	99.665	99.57
109	99.66	99.56
110	99.63	99.53
111	99.63	99.53
112	99.59	99.49
113	99.65	99.55
114	99.66	99.56
115	99.67	99.57
116	99.64	99.54
117	99.60	99.50
Av.	99.64	99.54

The new figures are 0.1 per cent lower than the former ones, but are still far from agreeing even with the total aluminium of the metal sample. The discrepancy can be explained as due either to contamination of the hydrogen with air, to large errors in the analysis of the metal sample, or to the wrong value having been used (27.1) as the atomic weight of aluminium.

With regard to the hydrogen, such evidence as has been produced indicates that it carries no more gaseous impurities than were present in the apparatus at the start of a determination, to which attention was drawn in the original paper.

The analysis of the metal used has been checked in this laboratory with satisfactory closeness, considering the small amount of sample which was at hand, so that there is no doubt of the accuracy of the original analysis of Rhodin, within the limitations of the methods he used.

The author believes it is the atomic weight of aluminium which is at fault. Although Mr. Churchill says, "The author had adduced no evidence to the effect that the accepted value for the atomic weight of aluminium is in error," it is of interest to note that in Mr. Churchill's last paragraph but one, he himself has to use a value other than the accepted one in order to bring the "metallic aluminium content" into agreement with the figure which would be shown if aluminium had been found by difference.

Since the publication of this article some metal of much higher purity and more trustworthy analysis has been obtained, against which apparatus and method are to be checked up.

Julian H. Capps

Bureau of Mines Experiment Station
Pittsburgh, Pennsylvania
October 31, 1921

Volume Increase of Compounded Rubber under Strain, and Recent Development in the Art of Rubber Microsectioning—Correction

In the articles by Henry Green of the above titles, appearing in the November and December 1921 issues of This Journal, the following errors occur:

Page 1030, 1st column, 3rd line from bottom, "microscopically" should read "macroscopically."

2nd column, 3rd line from bottom, $V = 4/3\pi\, a \times a \times a$ should be written $V = 4/3\, a \times a \times a$

Page 1131, 1st column, line 14, Fig. 1, *n* should read Fig. 1, *o*; line 18, *o* should be *n*.

Page 1132, 2nd column, line 2, "sulfur dioxide" should read "sulfur chloride."

SCIENTIFIC SOCIETIES

Fourteenth Annual Meeting of the American Institute of Chemical Engineers

The keynote of the meeting held at Baltimore, Md., December 6 to 9, 1921, was very obviously Gas Warfare and Chemical Preparedness. Most of the papers were on this general subject and the best attended and most interesting excursion was that to Edgewood Arsenal on the second day of the meeting.

The meeting opened on Tuesday morning at 9:15 at the Emerson Hotel with President David Wesson in the chair. The entire morning was devoted to a business session. The secretary reported the total membership as 529, an increase of 74 during the year. To meet the high cost of printing an assessment of $5.00 for active members and $2.50 for junior members had been voted by the Council for the coming year. After discussion the decision was reached not to make a permanent increase in dues. The Council also reported an amendment to the Constitution providing for Student Chapters similar to those affiliated with other engineering societies. By another resolution provision was made for the organization of local sections of the Institute.

Arthur D. Little, chairman of the Committee on Chemical Engineering Education, presented a very carefully prepared study of the courses in Chemical Engineering offered in all the technical schools and universities of the United States. Printing of this report was authorized, as was also the calling of a meeting of representatives of all institutions offering courses in Chemical Engineering, for the purpose of securing greater uniformity in courses offered.

The Committee on Atmospheric Pollution rendered a final report on pollution arising from sulfur dioxide fumes, stating that this problem had been solved by the investigation carried out by Dr. P. J. O'Gara, head of the Department of Agriculture and Smelter By-Products Investigation of the American Smelting and Refining Co., Salt Lake City, Utah. The results of this investigation will be published in the near future.

The election of officers for the coming year resulted as follows: Henry Howard, *president;* H. S. Miner, *third vice president;* John C. Olsen, *secretary;* F. W. Frerichs, *treasurer;* Chas. F. McKenna, *auditor;* Wm. H. Bassett, A. C. Langmuir, Alfred H. White, and A. E. Marshall, *directors.* By advance from second and third vice president, A. W. Smith became first vice president and Hugh K. Moore, second vice president.

The summer meeting is to be held in Buffalo and Niagara Falls in the latter part of June.

The most important resolutions passed were the following on the dye situation:

Whereas, the American Institute of Chemical Engineers assembled at its annual meeting at Baltimore, December 8, 1921, being convinced of the necessity of the embargo on dyes and synthetic organic chemicals as a measure essential for national defense and for the protection of the American Chemical Industry and holding, contrary to the belief of some, that this cannot be attained and regulated even by a very high protective tariff,

Therefore it hereby directs its officers to present this situation and this conclusion of the American Institute of Chemical Engineers to its representatives in Washington.

And the following on Chemical Warfare:

Be it resolved by the American Institute of Chemical Engineers in convention assembled in Baltimore, Md., December 8, 1921, that the following be sent to the American Delegation to the Conference on the Limitations of Armaments, the Advisory Committee thereof, and to our Senators and Representatives in Congress,

The campaign for the abolition of the use of gas in warfare is largely based on ignorance,

As Patriotic Americans, whose training and experience have been such as to enable us to better understand such technical matters, we state that chemical warfare is *now* much more humane than the older types. It is moreover the only type of warfare to which research and progress offer an almost certain promise of becoming still more humane,

We call attention to the fact that research in and preparation for gas warfare could be largely conducted secretly by an unscrupulous nation. The manufacture of many war gases is part of peace time industry. Effective chemical disarmament is therefore impossible,

In case of a life and death struggle between powers, we believe gases will be used, as gases represent real progress in the art of war, and you cannot arrest the hand of progress by rules and regulations,

We therefore urge for the proper defense of our country the imperative necessity of maintaining our Chemical Warfare Service.

President Wesson's address introduced the Symposium on Chemical Engineering and National Defense. In a paper on "Explosives and Fertilizers," Prof. Alfred H. White emphasized the urgent necessity of providing an adequate supply of fertilizers in order to maintain the fertility of our soils, which are rapidly being depleted. Dr. Raymond F. Bacon pointed out the humane aspects of gas warfare and the impossibility of its effective prohibition. The same point of view was taken by Maximilian Toch in a paper on "Chemistry and the Next War."

In discussing "Fundamental Research in Conservation and Defense," Mr. H. E. Howe called attention to a number of problems of fundamental importance which await solution. Dr. Robert M. Yerkes of the National Research Council explained the Research Information maintained under his direction.

In "The Chlorine Industry as an Essential Factor in our National Defense," Benjamin T. Brooks reviewed the capacity of the United States, for the production of chlorine, its uses, storage and transportation. Major Edward Holmes gave a similar survey of the lime industry.

In "Some New Products from Petroleum," Prof. J. H. James erported the results of a number of experiments on the distillation of low-grade petroleum products under oxidizing conditions.

A. E. Marshall discussed "Glass as a Material for Chemical Use," describing a number of installations in which this material has been successfully used and also the great possibilities for the employment of a glass having the properties of pyrex. In his paper on "Regenerative Evaporation," W. L. Badger presented a history of the attempts to utilize low pressure steam after compression in evaporators. Professor Badger pointed out the many difficulties to be overcome before this method would become commercially profitable.

Prof. Cavalier of France, exchange professor at the Johns Hopkins University, read a paper on the "Developments of the Chemical Laboratories in France," and showed a number of photographs of these laboratories under working conditions.

At a joint meeting with the Maryland Section of the American Chemical Society at the Johns Hopkins University on Thursday evening, Prof. J. C. W. Frazer explained the results obtained in the development of a catalyst by which carbon monoxide could be oxidized at room temperature to carbon dioxide. A gas mask had been developed utilizing this material. Prof. R. W. Wood showed a number of very interesting and very amusing applications of ultraviolet light.

The program of excursions was unusually complete; most of the chemical industries of Baltimore were open for inspection. On Wednesday afternoon the Curtis Bay industries were visited, including the plants of the U. S. Industrial Alcohol, The American Refractories, and the Davison Chemical companies. The greatest interest was shown in the experimental unit for drying air by means of silica gel and the freezing of water in a vacuum, the moisture being absorbed by silica gel.

More than 200 took the trip to Edgewood Arsenal. The entire morning was spent in inspection of the large installation of Nelson chlorine and caustic cells, the multiple effect evaporators, the gas mask factory, and the very extensive research laboratories. Luncheon at the Arsenal was followed by an address on Chemical Warfare by Brigadier General Amos A. Fries. After luncheon a field demonstration of all forms of gas warfare was witnessed with the greatest interest by the party.

On Friday afternoon a number of visits were made by small groups to various chemical plants, the largest party inspecting the large plant of the Baltimore Copper Works and the plant of the Standard Oil Company. At the latter plant the greatest interest was shown in the construction and operation of the improved Burton stills.

The social features of the meeting included a "Get-Together" at the Engineers' Club, at which a musical program was rendered, followed by dancing and a buffet supper. On Wednesday evening the ladies and members of the Institute and their guests attended a theater party tendered by the local committee and the local chemical industries. The subscription dinner was held on Friday evening at the Hotel Emerson.

In attendance and interest the meeting was the best which the Institute has ever held.

J. C. Olsen

Polytechnic Institute
Brooklyn, N. Y.

Officers of the Iowa and New York Sections of the A. C. S.

The officers of the Iowa Section for 1922 are as follows:

Chairman: Edward Bartow, Iowa City
Vice Chairman: R. W. Getchell, Cedar Falls
Secretary-Treasurer: L. Chas. Raiford, Iowa City
Councilor: J. N. Pearce, Iowa City

The recently elected officers of the New York Section are:

Chairman: Martin Hill Ittner
Vice Chairman: C. A. Browne
Secretary-Treasurer: B. T. Brooks
Executive Committee: R. H. McKee, Chas. H. Herty, J. E. Teeple, H. G. Sidebottom

Mr. Arthur H. Gallun

The following Resolution on the death of Mr. Arthur H. Gallun has been adopted by the Milwaukee Section of the American Chemical Society.

Whereas: In the death of Arthur H. Gallun, on November 9, 1921, the Milwaukee Section of the American Chemical Society recognizes the loss of one of its most valued members, who for the past eight years strove to make the Section an instrument of service for the general good, who by his substantial support assured the success of the work of its Library Committee, who was quick to aid the deserving and needy, who was active in the organization of the Leather Division of the American Chemical Society and had labored over plans for a tanning school that should bring about the coöperation of the best in both chemistry and industry, who was a staunch supporter of scientific research and encouraged the laboratories of his own plant to contribute to the development of chemistry, who generously endowed chemical research at Columbia University to be published without restriction, and who was a man much loved and admired by the Section.

Therefore, be it resolved that the Milwaukee Section of the American Chemical Society wishes to express its very deep sorrow on the loss of so valued a member and benefactor of science and to extend to his wife its most sincere sympathy.

The Birmingham Meeting of the American Chemical Society

The date at which the 63rd Meeting of the American Chemical Society will be held in Birmingham, Alabama, has been fixed as April 4 to 7, 1922.

. . . .

The Chairman and Secretary of the Cellulose Section are carefully considering the advisability of arranging for a meeting of that Section at Birmingham in April. The South is probably the largest cellulose-producing section of the country, and it should therefore be possible to have an enthusiastic meeting to listen to and discuss papers on cellulose and its derived products. It is requested that anyone planning to present a paper before this Section advise the secretary at once, even though the exact title may not be available until later. This request is made so that it can be ascertained whether a sufficient number who are interested in cellulose plan to attend the Birmingham Meeting of the Society to warrant holding a meeting of the Cellulose Section. The secretary's address is Gustavus J. Esselen, Jr., 248 Boylston St., Boston 17, Mass.

Nichols Medal for 1921

The Committee on the Nichols Medal Award met December 16 and decided not to award the medal for 1921. The retiring committee recommends to the 1922 committee that the last four numbers of the *Journal of the American Chemical Society*, which were not before them, be considered as a part of the 1922 chemical literature.

Calendar of Meetings

American Institute of Mining and Metallurgical Engineers—Spring Meeting, New York, N. Y., week of February 20, 1922.

American Ceramic Society—24th Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922.

American Chemical Society—63rd Meeting, Birmingham, Ala., April 4 to 7, 1922.

A. C. S. Officers for 1922

The newly elected officers of the Society are:

President: Edgar F. Smith.

Directors: M. C. Whitaker, W. R. Whitney.

Councilors-at-large: A. M. Comey, E. C. Franklin, W. D. Harkins, W. Lee Lewis.

WASHINGTON LETTER

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

THE REDUCTION OF ARMAMENTS CONFERENCE

The Far-Eastern situation, one of the most important problems of the Washington conference, has been clarified, if not settled for the next ten years, by the Four-Power Treaty between the United States, England, France, and Japan, which the Senate has already begun to debate. The reduction of armaments proposal made by the American delegation seems to be near acceptance.

Chemical warfare, however, has not yet been considered by the conference itself, although the committee of technical advisers, which considered chemical warfare and made studies for the delegates to the conference, has practically finished its work. This committee consisting of Dr. Edgar F. Smith, President of the AMERICAN CHEMICAL SOCIETY, chairman; Brig. Gen. Amos A. Fries, Chief of the Chemical Warfare Service, U. S. A.; Col. W. H. Bartholomew, Great Britain; Prof. Charles Moureu and Prof. A. Mayer, France; Lieut. Col. N. Pentimalli, Italy; Maj. Gen. H. Haraguchi, Japan, has made its report to the heads of delegations but its recommendations probably will not be made public for at least a week.

While it is generally believed that the report of the technical committee on chemical warfare is favorable to that mode of fighting, current press reports state that it is understood that the complete abandonment of all forms of chemical warfare has been recommended to the American Arms Conference delegation by its official Advisory Committee. The Associated Press report says: 'The Advisory Committee report was drawn by General Pershing and there is some intimation that it does not reflect the views of all other high army officials. In general, army officers are inclined to believe that poison gas or any other form of chemical warfare should be treated as any other military weapon." It is regarded as possible that the question of chemical warfare will not come directly before the conference, but that it will be referred to a continuing commission for study after the conference adjourns.

THE SENATE DYESTUFFS INVESTIGATION

The dyestuffs industry in the United States and the activities of importers of German dyestuffs will be investigated by the Senate Committee on the Judiciary as the result of a resolution introduced by Senator King of Utah, and passed by the Senate. The resolution directs the investigation of the alleged lobbying activities of both the American and German dye manufacturers. As originally introduced, it was directed at only the alleged American dyestuffs monopoly, but the insistence of Senator Frelinghuysen of New Jersey led to the inclusion of the importers of German dyestuffs. He charged that Germany is seeking by secret means to regain her control of the American dyestuffs market, and that a "carefully organized and strongly financed movement" is at work to this end. He urged a permanent embargo against German dyestuffs, and said that already there are in New York waters ships loaded with the German product waiting to unload, once the embargo provided for in the Emergency Tariff law is removed.

Senator Moses, in supporting the original King resolution, showed a large map with a circle containing the word "du Pont" located at Wilmington, Delaware. With radiating spider-like lines from this circle, he diagramed his conception of the extent of the control exercised by the alleged American dye monopoly.

"Representatives of the du Pont interests," said Senator Moses, "are connected with the League of Nations, the administration of the Versailles Treaty, the office of the Alien Property Custodian and other organizations." He also implicated various scientific societies and research organizations in and out of the Government.

SUSPENSION OF PUBLICATION OF GOVERNMENT PERIODICALS

A group of important scientific periodicals of the Department of Agriculture have suspended publication owing to the failure of Congress to give specific authority for their continuance after December 1, the date set by a provision of the Sundry Civil Act of March 4, 1921, for the suspension of all government department periodicals except those approved by Congress prior to December 1.

A resolution empowering the Congressional Joint Committee on Printing to authorize the continuance or discontinuance of these periodicals passed the Senate but did not come to a vote in the House before the adjournment of the last session of Congress. Therefore some forty-one publications issued by the government departments suspended publication, in most cases without even the customary obituary notice.

From a scientific standpoint, of those that are suspended, four Department of Agriculture publications are the most important: *The Experiment Station Record, The Journal of Agricultural Research*, the *Monthly Weather Review*, edited from the Weather Bureau, and *Public Roads*. Four other Department of Agriculture periodicals were doing a real service. The *Weekly News Letter* kept the 106,000 collaborators and employees of the department in touch with its activities and served to take current information to those especially interested in agriculture. Weather data were carried promptly by the weekly *National Weather and Crop Bulletin*. The weekly *Market Reporter* and the *Monthly Crop Reporter* went to those interested in agricultural statistics.

By the suspension of the forty-one periodicals, it has been estimated that from $500,000 to $1,000,000 will be saved each year. But scientists feel that this is false and mistaken economy. It is not inconceivable that even the temporary suspension of the quartet of periodicals mentioned may cause a much greater loss to the country than the supposed saving on the entire forty-one periodicals.

The inability to publish the results of important governmental researches, even excluding the suspension of the scientific periodicals, is becoming a serious situation. Printing appropriations of practically all governmental scientific bureaus have been badly cut and only the manuscripts that are most important can be published. Even these are usually many months in appearing.

HELIUM AS A BALLOON GAS

The flight of the navy dirigible, C-7, filled with helium, over Washington on December 5 was the first practical test of helium as a balloon gas on a large scale. This event will undoubtedly prove the beginning of a new era in lighter-than-air aviation, and it is a striking climax to four years of work by government chemists and engineers, largely directed by Dr. R. B. Moore of the Bureau of Mines. Helium has been raised from a chemical curiosity to a practical gas which surpasses hydrogen by being absolutely safe. The National Advisory Committee for Aeronautics, in its annual report, has just recommended that the Government acquire and seal for future use the best helium-producing gas fields, that the development of an efficient and economical process for the extraction and repurification of helium be continued, and that the Government inaugurate without delay the use of airships inflated with helium.

ANNUAL DEPARTMENTAL REPORTS

"The past year has been remarkable," says Brig. Gen. Amos A. Fries, Chief of the Chemical Warfare Service, in his annual report to the Secretary of War, "for the growth of understanding of the fundamental importance of chemistry in peace and war. With that growth has come a realization that the activities of peace and the activities of war are no longer capable of complete segregation." He pointed out that chemical warfare materials, as well as high explosives, are fundamentally bound up with the synthetic organic chemical industry.

The annual report of the Bureau of Chemistry of the Department of Agriculture tells of the work that has been done in studying processes used in industries related to agriculture. Some of the problems reported upon are: Making adhesives, cellulose, furfural, etc., from corncobs; manufacturing starch from potatoes; manufacturing a palatable sirup from the sweet potato; utilizing waste oranges and lemons; improving methods of tanning and testing leather; manufacture of rosin and turpentine; and study of the laws that govern the chemical reactions employed in the dye industry.

The annual report of the Commissioner of Patents for the fiscal year ending June 30, 1921, shows an increase of 34 per cent in the number of applications and an increase of 85 per cent in trade-mark applications. There were at the end of the fiscal year 49,334 patents awaiting action out of a total number of applications of 84,248. It also showed that the office had lost 163 scientifically and legally trained examiners, some of whom have been replaced by inexperienced men. The report as a whole pictured the deplorable condition of the Patent Office.

A new division in the Department of Commerce has been established to consider simplified commercial practices. It will be a subdivision of the Bureau of Standards, with William A.

Durgin of Chicago in charge. The work of the division will be devoted entirely to the elimination of waste as applied to commercial practices.

According to the latest figures there is a better trend in chemical exports of this country, but the volume of commodities in this group which are going abroad is still one-third of the volume for the corresponding period of a year ago. With the possibility of tariff legislation there has been a decided increase in the imports. The volume of trade, however, is still very much less than it was a year ago.

The Senate Finance Committee is at present considering individual schedules of the Tariff Bill and will continue to do so until some time next month. Further action on the chemical phases of the tariff cannot be expected until then or later.

It is believed here that the Secretary of War will recommend to Congress favorable action on Henry Ford's proposal to develop Muscle Shoals and that Congress will receive the definite plan shortly.

The Tariff Commission has been requested by the Senate Finance Committee to prepare for its use a volume similar to the Summary of Tariff Information compiled for the House Ways and Means Committee last January.

The U. S. Geological Survey's Commercial Atlas, Part II, will be issued about Jan. 1. This will give the distribution of developed and undeveloped water power throughout the world. Part III will deal with resources of mineral fuels and Part IV with the reserves of the principal metals.

December 14, 1921

LONDON LETTER

By Stephen Miall, 157 Haverstock Hill, Hampstead, N. W 3, England

Industrial conditions here still form a large proportion of our thoughts, and we have now all made up our minds that a recovery is beginning and will be very slow and irregular in its growth. In this country and probably in this continent we can look forward to another year of poor trade and much unemployment. But all this is part of the natural cycle; riches beget pride, pride begets war, war begets poverty, poverty begets industry, industry begets riches, and so on. We are now in the state of poverty but here we are trying to live within our incomes and as a nation we shall succeed in doing it this year or next year or sometime. Our trouble is that some of our neighbors have not yet got so far as we have. Russia has ceased to have any income, Austria has so overspent her income that her currency is bought by the kilo, Poland can hardly buy anything and is not emerging yet from its considerable impecuniosity and Germany, formerly our best or nearly our best customer in many industries, seems to be going on the same path as Austria and Poland. Before the war Germany did not raise enough money to cover her national expenditure, during the war of course no effort was made to do this, and since the armistice she has probably been both unable and unwilling to make the attempt. The issue of paper money on a large scale is analogous in some respects to the issue of bonus share certificates by the company which is not very prosperous, and there is bound to come a time either in six months or some other number of months when this issue by Germany must stop. Five years ago it would have been incredible that Russian rubles should be worth only the paper they were printed on, and I suppose that Germany will at any rate stop printing marks when it costs more to print them than they will fetch. The time will surely come, and it seems to many of us not very far off, when the government of that country will find it impossible to carry on with the present financial methods. Then there will be political and labor troubles and Germany will find herself where we are now—poor, overtaxed, and faced with considerable unemployment. She is having her trade boom now; we had ours two years ago; both were overdone and to some extent unreal. How much of the profit or loss is a mere question of bookkeeping is hard to say. Ten years ago I owned ten houses worth £300 each, three years ago they were worth £550 each, now they are worth £450 each. Am I in fact any richer than I was? The same sort of delusion goes on in Germany at the present time; a man buys a ton of some chemical compound for say 20,000 marks, the next day it is worth 22,000 marks, and a fortnight afterward 30,000 marks. It may pass through many hands and everyone concerned makes a bookkeeping profit, and he and all his friends repeat the transaction to the utmost of their means and to their entire satisfaction. It seems as if the only way of avoiding a heavy loss in Germany is for each man to buy goods to the utmost extent of the credit he has, and he complacently thinks he is becoming richer. Surely one of these days they will wake up! I met recently in Geneva at the International Labor Conference some Germans whose expenses were about £3 sterling per day or at the present rate of exchange 30,000 marks per day. How long can the Germans continue to travel in other countries? Another man I heard of recently spent a holiday in Austria and had hard work to spend about £10 in three weeks, I mean he had to order expensive wines and luxurious dishes. We have become, whether we like it or not, a collection of more or less self-supporting states, and it is difficult to know whether, when we impose duties on chemicals imported from Germany, we are making the situation worse or merely making it easier for people to endure what is in fact a disagreeable necessity.

ORGANIZATION OF FEDERAL COUNCIL

We are trying to do here what you seem to have done very efficiently in America, that is, so to organize British chemistry that chemist as a whole can make their voice heard and influence felt. The Chemical Society, the Society of Chemical Industry, the Association of British Chemical Manufacturers, the Faraday Society, the Public Analysts, the Dyers and Colorists and the other societies have appointed representatives to form a Federal Council, which is gradually getting into working order. But it is too recent a creation to make its influence felt in government circles; otherwise the Safeguarding of Industries Act—so far as chemicals are concerned—would have been very different. This country professes to be a democracy disguised as a monarchy; it is in fact a bureaucracy mainly recruited from an aristocracy; the officials who do the actual governing are usually about as sympathetic to science as stockbrokers or brigadier generals. In Parliament the men who understand chemistry and its needs could be numbered on one's fingers and most of these are naturally put into positions where their knowledge will not be liable to bias their views. Thus Sir Alfred Mond, who knows a good deal about the chemical industry, is in charge of the Ministry of Health; if Sir Joseph Thomson or Sir Ernest Rutherford were successful politicians we should probably find them Colonial Secretary and Director of Poor Law. The average politician seems to regard the chemist as something between an alchemist and a druggist—a clever crank, to be listened to with the courtesy the government official is accustomed to display, but who may be forgotten so soon as his back is turned. The Federal Council hopes that in time it may be able to keep the country on the right track in matters pertaining to chemistry.

November 15, 1921

Review of Scientific Instruments

A number of scientists have felt a need for adequate reviews and descriptions of scientific instruments. For some months the matter has been discussed by those interested, including the makers of apparatus, the National Research Council, the Bureau of Standards, and the Optical Society of America.

Arrangements have now been completed whereby the *Journal of the Optical Society of America* will add to its name "*and Review of Scientific Instruments*," devoting a section to such reviews in addition to its regular editorial pages. The first number of the expanded journal is to appear April 15, 1922, and monthly thereafter.

Paul D. Foote, Bureau of Standards, is editor-in-chief, and F. K. Richtmyer, Cornell University, assistant editor-in-chief.

The Mineral Potash Corporation has been chartered under the laws of Maryland with a capitalization of $700,000 to begin the building and operation of a plant for the manufacture from powdered feldspar of an abrasive for polishing metals, enamels, and household goods. The lands upon which the feldspar deposits are located are at Ilchester, Howard County, Maryland.

OBITUARY

Joseph William Richards

J. W. Richards

Joseph William Richards was born in Oldbury, Worcestershire, England, on July 28, 1864. He came to this country in 1871, attended the public schools of Philadelphia, Pa., and subsequently received the following degrees from Lehigh University: A.C. (analytical chemist) in 1886; M.S. in 1891 and Ph.D. in 1893. In 1886 and 1887 he was employed in his father's metal refinery at Philadelphia, after which he was continuously employed in teaching at Lehigh University up to the time of his death. He was one of the founders of the American Electrochemical Society; its first president, 1902–3, and secretary 1907–1921. He held many offices in other societies and especially in the American Institute of Mining and Metallurgical Engineers, with which he was officially connected for more than a dozen years as councilor, director, and vice president; for seven years he was chairman of its Iron and Steel Committee. He was also appointed in several public capacities, such as member of the Engineering Council, Engineering Foundation, American Engineering Standards Committee, Engineering Division of the National Research Council, Naval Consulting Board; president of the Chemical Section of the Franklin Institute and its professor of electrochemistry for three years; member of the U. S. Assay Commission, member of the Jury of Awards, Department of Chemistry, National Export Exhibition, Philadelphia; member Jury of Awards and chairman of subjury on Metallurgy, Panama-Pacific International Exposition.

His most important books were a "Treatise on Aluminum," which is the established authority on this subject in English, and three small volumes on "Metallurgical Calculations" which have been translated into five foreign languages. He was also a voluminous contributor to technical literature by monographs and discussions.

His chief interest outside of his professional work was fondness for travel, a sympathetic taste for music and languages, and a deep interest in the study of religious and philosophic subjects. He was noteworthy for a seemingly tireless capacity for painstaking work, but in his relations to others he exhibited always a gentlemanly courtesy and an unselfish devotion to upbuilding the interests of engineers and chemists.

Bradley Stoughton

PERSONAL NOTES

President Edgar F. Smith, provost emeritus of the University of Pennsylvania, has been elected an honorary member of the Société de Chimie Industrielle, and also an honorary member of the Chemical, Metallurgical and Mining Society of South Africa.

Sir William Pope has been awarded the "Grande Médaille" and **Dr. F. G. Cottrell** has been elected an honorary member of the Société de Chimie Industrielle.

Dr. Ernest Fox Nichols has resigned the presidency of the Massachusetts Institute of Technology and his resignation has been accepted by the executive committee of the corporation. His decision resulted from the unfavorable condition of his health. Dr. Elihu Thomson, of Swampscott, chief consulting engineer of the General Electric Company, who served as acting president after the death of President Richard C. Maclaurin in January 1920, has again been appointed to that position.

Mr. Reuben L. Lindstrom, superintendent of the Point St. Charles Plant, Canadian Steel Foundries Ltd., died Dec. 12, 1921, at his home in Montreal. He left the Bettendorf Co., Bettendorf, Iowa, four years ago to become metallurgist with the Canadian Steel Foundries Ltd., a position which he filled until appointed superintendent of the St. Charles Works eighteen months ago.

Dr. J. A. Gunton has been appointed head of the chemistry department in Transylvania College, Lexington, Ky. Dr. Gunton recently received his doctorate of philosophy from the University of Illinois.

Mr. Lauchlin M. Currie resigned as research chemist with the Hooker Electrochemical Company at Niagara Falls to accept a position as assistant professor of mathematics in Davidson College, Davidson, N. C.

Mr. Paul R. Dawson, formerly teaching fellow in chemistry at the University of North Carolina, has accepted an appointment as assistant biochemist in the Soil Fertility Investigations, Bureau of Plant Industry, Washington, D. C.

Mr. W. S. Mahlie, formerly in the laboratory of the Buckeye Steel Castings Co., Columbus, Ohio, is at present employed as chemist and bacteriologist for the City of Fort Worth, Texas.

Mr. L. C. Humphrey has entered the graduate school at the University of Minnesota, Minneapolis, Minn., and will take advanced work in chemistry toward the doctorate degree. He will also do some assisting in the School of Chemistry. Mr. Humphrey, previous to September 1, was instructor in chemistry at Montana State College, and was also in charge of the Montana Oil Laboratory at Montana State College, Bozeman, Mont.

Dr. Austin Bailey, who has recently been employed as superintendent of the apparatus division of the Corning Glass Works, Corning, N. Y., has resigned his position to accept an assistant professorship in the physics department at Kansas University, Lawrence, Kans.

Mr. R. F. Remler, formerly assistant chemist in the nutrition department of the Ohio Agricultural Experiment Station, Wooster, Ohio, now holds an Industrial Fellowship at the Mellon Institute of Industrial Research, Pittsburgh, Pa.

Mr. R. E. Wilkin, after receiving his master's degree at the University of Iowa, Iowa City, Iowa, resigned his assistantship there to accept a position as instructor in chemistry at Kansas State Agricultural College, Manhattan, Kans.

Mr. John Jos. Gorrell, who has been connected with the Technical Direction Bureau of the Aluminum Company of America, New Kensington, Pa., has accepted a position as analytical chemist with the Cambria Steel Co., Johnstown, Pa.

Mr. S. G. Byam, chief chemist at the Fairfield Rubber Works of E. I. du Pont de Nemours & Co., has resigned from that position to become chief chemist with entire charge of the technical development at the Plymouth Rubber Co., Canton, Mass.

Mr. Parry Borgstrom, formerly research associate at the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., is now instructor in physiological chemistry, Tulane University Medical School, New Orleans, La.

Mr. John H. Waldo has left Illinois, where he received his undergraduate work and master's degree, to assume the position of assistant professor in chemistry and physics in Morningside College, Sioux City, Iowa.

Dr. Clarence J. Monroe recently received his Ph.D. degree from the University of Chicago, Chicago, Ill., and has been appointed assistant professor in physical chemistry at the Missouri School of Mines and Metallurgy, Rolla, Mo.

Mr. Jas. A. Holladay was recently transferred from the Niagara Works of the Union Carbide and Electro Metallurgical Companies to take up work with the Union Carbide & Carbon Research Laboratories, Inc., Long Island City, N. Y.

Mr. Joseph P. Grennan, head of the department of chemistry in the Charles M. Schwab Laboratories at St. Francis College, Loretto, Pa., is now professor of analytical chemistry at Gonzaga University, Spokane, Wash.

Mr. A. C. Reed, who resigned as assistant materials engineer from the Navy Department, Bureau of Construction and Repair, last June, now holds a similar position with the department of maintenance and repair, Emergency Fleet Corporation, New York City.

Mr. Lincoln T. Work has been appointed instructor in chemical engineering at Columbia University for the year beginning October 1. Mr. Work completed three years of graduate work in this department at Columbia last June.

Miss Omega Hilton has discontinued work as chemist of the American Nitrogen Products Company to take a position as instructor in pharmacy at the University of Washington, Seattle, Wash.

Miss Ruth O'Brien recently returned to the chemistry department of Iowa State College, where she is associate professor of household chemistry, after a year's leave of absence which was spent working under Dr. Stieglitz at the University of Chicago.

Mr. D. B. Dill, who has been in charge of the San Diego branch of the Food Research Laboratory, conducting investigations in the canning of fish and the handling of fishery by products, has accepted a transfer to the Food and Drug Inspection Laboratory at Seattle, Wash., the Food Research Laboratory at San Diego having been discontinued.

Mr. L. J. Baney is at present superintendent of the Briggs Chemical Co., Amherst, Ohio, manufacturers of coal-tar products, having resigned from the Chemical Warfare Service at Edgewood Arsenal, Md.

Mr. Milton R. Louria, who completed his chemical engineering course at Columbia University last June, has been appointed instructor in chemistry at the University of Maine for the current year.

Mr. C. L. Hippensteel, following graduation from the School of Chemical Engineering of Purdue University, Lafayette, Ind., last June, accepted a position in the engineering department of the Western Electric Co., New York City.

Mr. F. H. Tucker has become associate chemist in the Bureau of Public Roads, Washington, D. C., having been connected with the Chile Exploration Company for the past year as research chemist in their New York laboratory.

Dr. Walter A. Lawrence, associate professor of chemistry at McMaster University, Toronto, has been appointed professor of chemistry and head of the department at Bates College, Lewiston, Me.

Mr. C. W. Botkin, who has been doing research on the refining of shale oil at the Colorado School of Mines for the past fifteen months, has accepted a position as head of the chemistry department in the New Mexico College of Agriculture and Mechanic Arts, State College, N. M.

Mr. E. Wertheim, formerly a graduate student at the University of Chicago, Chicago, Ill., has been appointed associate professor of organic chemistry at the University of Arkansas, Fayetteville, Ark.

Mr. Fred J. Allen recently received his M.S. degree from Purdue University and has returned to Corvallis, Ore., after a leave of absence, to resume his work as instructor in the chemistry department of the Oregon Agricultural College.

Mr. William U. Gallaher has been appointed chemist at the Illinois State Water Survey, Urbana, Ill., with the opportunity of pursuing further study at the University of Illinois. Mr. Gallaher received his degree of Master of Science from the University of Iowa last spring.

Mr. Frank Henry, formerly with the Dunlop Tire and Rubber Corp., Buffalo, N. Y., is at present with the Rochester Gas and Electric Corp., Rochester, N. Y., where he is doing research (chemical) work mainly on gas plant problems.

INDUSTRIAL NOTES

The executors of the estate of John C. Wiarda have sold the assets of their chemical manufacturing and jobbing business to Howard B. Bishop of 101 Park Ave., New York, who will continue the business under the name of John C. Wiarda & Co., Inc., and will enlarge and extend the manufacturing and jobbing facilities.

A special faculty research committee has been organized at Oberlin College to coöperate with the National Research Council. Dr. S. R. Williams, head of the department of physics, is chairman, while other members include members of the departments of mathematics, sociology, psychology, chemistry, and geology.

The main building of the Heyden Chemical Works plant at Garfield, N. J., was destroyed by fire on December 12, 1921, causing the death of four men and injuring several more. The fire was the result of an explosion, and within a few minutes the building was a mass of flames which spread to half a dozen other buildings and threatened nearby tanks of alcohol and explosive materials. The damage is estimated at more than $200,000. The plant was sold by the Alien Property Custodian about two years ago and purchased by A. A. Ryan for $1,500,000.

A huge pile of lava rock at Husum, Washington, which had for years harbored numbers of rattlesnakes was cleared recently by the use of mustard gas. The gas was freed in the porous formation through 150 ft. of garden hose and within half an hour the snakes blinded and half dead came out and were killed. Other communities have requested the gas for the same purpose.

The Dosch Chemical Co., organized in Delaware with a capital of $2,500,000, has purchased the property of the Bernheim Distilling Co., at Louisville, Ky., and will establish a large insecticide and spraying plant. The plant is to have four departments—manufacturing, research, public service, and advertising. Between 12,000,000 and 20,000,000 lbs. of low-grade tobacco will be used annually. A large variety of preparations used by agriculturists and horticulturists are to be produced, in addition to dusting machines and other equipment required in the use of insecticides. It is believed the plant will begin operations in January.

The building of the Calco Chemical Co., at Eggers' Station, N. J., was destroyed by fire recently, with an estimated loss of $50,000.

Statistics compiled by The Engineering Agency show that the number of inquiries for technical help in manufacturing construction, industrial and commercial work steadily decreased from February 1920 to June 1921, reaching a minimum in June, since when there has been a slow but comparatively steady increase. During the declining period many employers were forced to cancel their inquiries because of the falling off of their work, but since June there have been very few canceled inquiries.

After intensive research, the National Aniline and Chemical Company has established a rubber laboratory which will cooperate through consultation and advice with rubber factories. Through the efforts of this laboratory the National will be able to present products definitely standardized and especially adapted to rubber compoundings.

The Morris Fertilizer Company of Chicago has completed the construction and equipment of a modern high-grade hydraulic pebble phosphate mining plant at Bartow, Fla., where the company owns over 2000 acres of high-grade pebble phosphate running unusually low in its content of iron and aluminium. The company will specialize in the mining, washing, and drying of the material for export through the port of Tampa. Operations have already been begun and several cargoes have been shipped abroad. A complete laboratory and corps of chemists are maintained in order to have at all times analytical control of the rock mined and stored.

The Seydel Manufacturing Co., of Jersey City, N. J., has merged with the Nitro Products Corporation, Nitro, W. Va., to form the Seydel Chemical Co., the manufacturing base of which will be located at Nitro. The general offices and laboratories of the new company will be located at Jersey City. Herman Seydel, president of the Seydel Mfg. Co., is president of the Seydel Chemical Co.; the other officers are Paul Seydel and Frank C. Pitcher, vice presidents, and J. B. Pitcher, formerly president of the Nitro Products Co., secretary and treasurer.

GOVERNMENT PUBLICATIONS

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Metric System. Hearing before subcommittee on S. 2267, to fix metric system of weights and measures as single standard of weights and measures for certain uses. October 11–13, 1921. Part I. 50 pp.

TARIFF COMMISSION

Tariff Information Surveys. Revised edition, 1921.

C–16. On articles in paragraph 143 of Tariff Act of 1913 and related articles in other paragraphs. **Aluminium, magnesium, calcium, barium, sodium, and potassium, ores, metals, and manufactures.** 80 pp. Paper, 5 cents.

C–17. On articles in paragraphs 144 and 145 of Tariff Act of 1913 and related articles in other paragraphs. **Antimony, antimony alloys, and antimony salts.** 76 pp. Paper, 5 cents.

C–21. On articles in paragraphs 152 and 153 of Tariff Act of 1913 and related articles in other paragraphs. **Lead.** 63 pp. Paper, 5 cents.

FL–21. On articles in paragraphs 518–537 of Tariff Act of 1913 and related articles in other paragraphs. **Iron ore, pig iron, and scrap.** 103 pp. Paper, 10 cents.

N–20. On articles in paragraph 367 of Tariff Act of 1913 and related articles in other paragraphs. **Asbestos.** 56 pp. Paper, 5 cents.

C–19. On articles in paragraphs 147–150 of Tariff Act of 1913 and related articles in other paragraphs. **Copper and copper alloys.** 100 pp. Paper, 10 cents.

C–23. On articles in paragraph 155 of Tariff Act of 1913 and related articles in other paragraphs. **Nickel ore, matte, metal, and manufactures** 32 pp. Paper, 5 cents.

C–25. On articles in paragraphs 159 and 160 of Tariff Act of 1913 and related articles in other paragraphs. **Quicksilver.** 30 pp. Paper, 5 cents.

FL–6. On articles in paragraphs 403–408 of Tariff Act of 1913 and related articles in other paragraphs. **Arsenic and other articles.** 56 pp. Paper, 5 cents.

FL–10. On articles in paragraphs 447–457 of Tariff Act of 1913 and related articles in other paragraphs. **Coal and coke.** 56 pp. Paper, 5 cents.

FL–20. On articles in paragraph 517 of Tariff Act of 1913 and related articles in other paragraphs. **Platinum, platinum metals, gold and silver.** 70 pp. Paper, 5 cents.

WAR DEPARTMENT

Air Service

Thermometers. Laboratory test on Hartmann & Braun electric thermometer. Equipment Section Report. 4 pp. 1921. (Air Service Information Circular, Aviation, 3. No. 277, October 1, 1921.)

PUBLIC HEALTH SERVICE

An Occupational Dermatoconiosis among Zinc Oxide Workers. J. A. TURNER. Public Health Reports, 36 (November 4, 1921), 2727–32. The following conclusions are drawn from this study: Zinc oxide is considered a nontoxic substance, and from the chemical analysis it is evident that the adulterating substances are in insufficient amount to be harmful. It is a nonpoisonous material, but is capable of acting as a mechanical conveyor of bacteria. The zinc oxide, body debris, and bacteria are forced into the sebaceous glands, distending them. This action is aided by free perspiration and the rubbing together of two body surfaces. It is probable that the presence of the foreign substances, and the increased tension due to the retained secretion, produce sufficient irritation of the gland walls to allow an invasion of the bacteria and a resulting infection.

The Treatment of Leprosy with Chaulmoogra Oil. Public Health Reports, 36 (November 11, 1921), 2769–70. In regard to the treatment of leprosy with the ethyl esters of chaulmoogra oil it is stated that their use has resulted in the apparent cure of the disease in a considerable number of cases, but whether these "apparent cures" be permanent or not is a matter which requires time to determine. The results have, however, led to the belief that a therapeutic agent has been developed which surpasses in value everything which has been brought forward up to the present time.

DEPARTMENT OF THE INTERIOR

General Land Office

Potash Regulations under Act of October 2, 1917. Approved March 21, 1918. Reprint with slight changes, 1921. Circular 594. 21 pp. The circular contains rules and regulations governing the issuance of permits authorizing exploration of public lands for potassium; form of permit authorizing exploration of public lands for potassium; regulations pertaining to leases for lands containing potash; form of application for lease; form of lease of potash lands; regulations for permits for camp site and refining works; form of use permit for camp site or refining works; patents for lands containing potash, and quotes in full the act authorizing exploration for and disposition of potassium.

GEOLOGICAL SURVEY

Iron Ore, Pig Iron and Steel in 1919. E. F. BURCHARD. Separate from Mineral Resources of the United States, 1919, Part I. 32 pp. Published October 14, 1921. The problem that confronted leaders in the iron and steel industry in the United States at the beginning of 1919 was readjustment from war-time to peace-time conditions. Iron-ore production decreased 13 per cent, a decrease of 1.6 per cent as compared with the production of the last pre-war normal year.

Zinc in 1919. C. E. SIEBENTHAL AND A. STOLL. Separate from Mineral Resources of the United States, 1919, Part I. 12 pp. Published October 13, 1921. The primary zinc produced from domestic ores in 1919 was valued at $66,032,000, based on the average selling price, as compared with $89,618,000 in 1918—a decrease of 26 per cent. The quantity decreased 8 per cent.

Stone in 1919. G. F. LOUGHLIN AND A. T. COONS. Separate from Mineral Resources of the United States, 1919, Part II. 37 pp. Published October 18, 1921. About 65,539,000 short tons of stone were sold in the United States in 1919, 4 per cent less than in 1918, and 22 per cent less than in 1917. The total value of the stone sold in 1919 was $96,709,143, a value greater than any previously recorded.

Feldspar in 1920. L. M. BEACH. Separate from Mineral Resources of the United States, 1920, Part II. 2 pp. Published October 29, 1921. The quantity of feldspar marketed in 1920 was 114 per cent greater than in 1919 and 53 per cent greater than in 1918.

Abrasive Materials in 1920. L. M. BEACH AND A. T. COONS. Separate from Mineral Resources of the United States, 1920, Part II. 5 pp. Published October 28, 1921. The following table gives the value of all abrasive materials consumed in the United States, 1916–1920:

	1916	1917	1918	1919	1920
Natural abrasives	$1,664,339	$2,385,165	$2,864,332	$2,887,902	$4,299,812
Artificial abrasives	2,935,909	8,137,242	6,940,000[1]	5,019,779[2]	6,269,084[2]
Imports ...	555,850	812,303	1,187,632	2,237,077	4,425,409
	5,156,098	11,334,710	10,991,964	10,144,758[2]	14,994,305[2]
Exports ..	4,452,741	6,621,884	6,056,242	6,138,366	7,025,621
Apparent consumption....	703,357	4,712,826	4,935,722	4,006,392	7,968,684

[1] Estimated and not including entire production during second half of 1918.

[2] Not including production of one large company.

Mineral Waters in 1920. W. D. COLLINS. Separate from Mineral Resources of the United States, 1920, Part II. 6 pp. Published October 29, 1921. The term "mineral water" as here used applies to water that is bottled and sold in its natural state or only slightly altered from its natural state. The statistics given refer only to domestic mineral waters that have been sold. Three uses of mineral waters are recognized—table use, medicinal use, and use in the manufacture of soft drinks.

Gold and Silver in 1919. General Report. J. P. Dunlop. Separate from Mineral Resources of the United States, 1919, Part I. 45 pp. Published October 31, 1921. Domestic smelters and refiners produced 2,918,628 fine oz. of gold and 56,682,445 fine oz. of silver from domestic sources in 1919, also 668,161 fine oz. of gold and 57,806,123 fine oz. of silver from foreign ores and bullion, an increase of 101,275 oz. of gold and 1,826,703 oz. of silver compared with the corresponding figures for 1918. The foreign ores came mainly from Mexico, Canada, and Peru.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1920. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1920, Part I. 6 pp. Published November 3, 1921. The ore mined and treated yielded in recovered gold 0.1668 oz. or $3.45 a ton, as compared with $3.65 a ton in 1919. The mills of the state treated 1,356,079 tons of ore, which yielded as bullion $4,673,514 in gold and 87,319 fine oz. of silver, valued at $95,178, an average recovery per ton of $3.45 in gold and 0.064 oz. in silver, as compared with $3.62 in gold and 0.086 oz. in silver in 1919. The lead produced in South Dakota in 1920 was 19,735 lbs. less than in 1919. No gold, silver, or copper was produced at mines in Wyoming in 1920.

Sand and Gravel in 1920. L. M. Beach. Separate from Mineral Resources of the United States, 1920, Part II. 10 pp. Published November 5, 1921. In spite of such hampering conditions as an insufficient supply of cars, the high cost of transportation, and the disorder of the local markets, the quantity of sand and gravel produced in the United States in 1920 increased 16 per cent and the value 43 per cent over 1919.

Lime in 1920. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1920, Part II. 11 pp. Published November 3, 1921. Although more lime was produced in 1920 than in 1919, the supply was not large enough to meet the demand. The shortage was not due to the inability of the plants to increase their output but to conditions beyond the control of the lime makers. Nearly all lime producers reported higher prices in 1920 than in 1919. There is every reason to predict better prospects for the lime industry.

Lead in 1920. General Report. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1920, Part I. 11 pp. Published October 14, 1921. The output of refined lead in the United States from domestic ores in 1920 was 476,849 short tons, valued at $76,296,000 at the average selling price of pig lead in New York, a gain, as compared with 1919, of 12 per cent in quantity and of 70 per cent in value.

Slate in 1920. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1920. Part II. 9 pp. Published October 12, 1921. The general industrial conditions in the slate industry in 1920 were seemingly somewhat better than in the three or four preceding years. Prices advanced for all slate products from 10 to 30 per cent, or enough to cover advances in labor and coal. The total quantity of mill stock sold in 1920 was an increase of 33 per cent over the quantity sold in 1919, but 24 per cent less than that sold in 1913, the record year.

Carbon Black Produced from Natural Gas in 1920. E. G. Sievers. Separate from Mineral Resources of the United States, 1920, Part II. 5 pp. Published October 13, 1921. The total quantity of carbon black produced from natural gas in the United States in 1920 decreased 1.4 per cent from 1919, notwithstanding an increase in the number of plants. In 1919 the plants were still operating at or near full capacity on account of the war, but since normal conditions have been restored the production has decreased. The output in 1920 was made by 19 producers. The prices received ranged from 4 to 27 cents a pound. The average daily production in 1918 was 119,178 lbs.; in 1919, 142,621 lbs.; and in 1920, 140,608 lbs.

BUREAU OF MINES

Selected Bibliography of Oil Shale. Compiled by E. H. Burroughs and M. J. Gavin. Reports of Investigations. Serial No. 2277. 66 pp. Published September 1921.

The Recovery of Unburned Fuel from Boiler Furnace Refuse. Thomas Fraser and H. F. Yancey. Reports of Investigations. Serial No. 2281. 3 pp. Published September 1921. It is believed that the recovery of unburned fuel from boiler furnace refuse by the use of concentrating tables would pay only in large plants. Considering the present freight rates, the saving of transportation charges on fuel recovered at the plant is obvious. Experiments conducted by washing on coal-washing tables, however, show that continuous operation of a one-table unit would be possible at a power plant producing 120 tons of refuse per 24 hrs.

Natural Gas-Gasoline Blends. D. B. Dow. Reports of Investigations. Serial No. 2279. 2 pp. Published September 1921. The most common blending material now used in the Mid-Continent field is a naphtha ranging in gravity from 50°–52° B., with an end-point of 450° F. or less.

Hot High-Nitrogen Gas in a Metal Mine. G. E. McElroy. Reports of Investigations. Serial No. 2282. 3 pp. Published September 1921.

The Utilization of Waste Slate as a Filler. Oliver Bowles. Reports of Investigations. Serial No. 2283. 5 pp. Published September 1921. All of the information available indicates that waste slate may be used to advantage as a filler in mechanical rubber goods and in some classes of oilcloths, floor coverings, and window shades. Apparently it is not adapted for use in rubber of a grade used in automobile tires. For plastic roofing and flooring products containing coal tar it has long been in use and constitutes a very satisfactory filler.

The Determination of Oxides of Nitrogen. V. C. Allison, W. L. Parker, and G. W. Jones. Technical Paper 249. 13 pp. Paper, 5 cents. 1921. This paper describes a method for determining small quantities of oxides of nitrogen, other than N_2O. It has been developed from the usual procedure of water analysis. With a 250-cc. sample as low as 10 parts of oxides of nitrogen (other than N_2O) per million parts of air can be determined with an accuracy of about 5 parts per million.

Production of Explosives in the United States during the Calendar Year 1920 with Notes on Mine Accidents Due to Explosives. W. W. Adams. Technical Paper 291. 44 pp. Paper, 5 cents. 1921. The production of explosives in the United States during the calendar year 1920 showed a marked recovery from the slump in 1919. The production (excluding exports) was 537,954,750 lbs., an increase of 120,320,280 lbs., or about 29 per cent, as compared with the preceding year. Of this 47 per cent was black blasting powder, 43 per cent high explosives other than permissible explosives, and 10 per cent permissible explosives. As compared with the year 1919, there was an increase of 41 per cent in the production of black powder, 15 per cent in "high" explosives, and 39 per cent in explosives classified as "permissibles."

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. Reports of Investigations. Serial No. 2284. 32 pp. Issued October 1921.

Rate-of-Production Curve and Its Application to the Valuation of Oil Properties. W. W. Cutler. Reports of Investigations. Serial No. 2285. 5 pp. Issued October 1921.

Bureau of Mines Experimental Tunnel for Studying the Removal of Automotive Exhaust Gas. A. C. Fieldner and J. W. Paul. Reports of Investigations. Serial No. 2288. 3 pp. Published October 1921. In coöperation with the New York and New Jersey State Bridge and Tunnel Commissions, the Bureau of Mines has just completed the construction of an experimental tunnel in the Bureau's experimental mine at Bruceton, near Pittsburgh, Pa. The purpose of this tunnel is to make a final study of the ventilation problems arising in the adequate ventilation of vehicular tunnels for automobiles and trucks.

Bentonite. R. B. Ladoo. Reports of Investigations. Serial No. 2289. 5 pp. Issued October 1921. Particular attention is directed to the commercial utilization of bentonite in paper making, as a filler in the manufacture of soap, as an ingredient in gypsum and lime plasters, as a superior adhesive paste, as a water softener, and its possible use to dewater crude petroleum.

Viscosities and Pour Tests of Typical Crude Oils from the Eastern and Rocky Mountain Producing Fields of the United States. E. W. Dean, A. D. Bauer, and W. B. Lerch. Reports of Investigations. Serial No. 2290. The figures which form a part of the report show that the crude oils from the eastern producing fields vary only moderately in viscosity and pour test. The pour test figures for the Rocky Mountain crude oils are noticeably variable.

Monthly Statement of Coal-Mine Fatalities in the United States, August 1921. W. W. Adams. 11 pp. Paper, 5 cents. 1921.

COMMERCE REPORTS

Statement comes from Chile that an agreement has been concluded between the Association of Nitrate Producers and European and American buyers and ratified by the producers on October 27, 1921, which set the prices of nitrate until July 1922. Shipments from Chile are not likely to increase greatly until the end of the year 1922 unless there is an improved demand for fertilizer in America and Europe. (P. 566)

There has been encouraging improvement in the British **tin-plate** trade. Total exports for August were the largest for any month since April. The local industry feels the competition of the United States in the foreign tin-plate markets, finding it difficult to combat owing partly to the high cost of production. (P. 569)

A market is reported in southern Sweden for **imitation leather.** This market is said to be able to import from the United States $268,000 worth annually. (P. 574)

The third series of articles on the **petroleum** industry in Mexico contains a list of the companies operating in Mexico, the production of oil by zones and companies, and the number and capacity of refineries, storage tanks, and pipelines. (Pp. 590–7)

The Czechoslovak Office of Foreign Trade has made the following reduction in export duties: Industrial **kaolin** not used in the manufacture of porcelain and ceramics reduced from one-half of 1 per cent to one-fourth of 1 per cent of the invoice price (Sept. 1, 1920). (P. 608)

The **copra** trade of the Pacific is reviewed, and the report is accompanied by tables showing the imports and exports of copra in tons for each of the importing and exporting countries of the Pacific, including British and Dutch Malaya. (Pp. 616–9)

The 1921 **olive** crop in southern Italy is estimated to be an increase of 50 per cent over that of last year. Ordinarily the proportion of oil varies from 20 to 40 per cent, according to the quality of the fruit. (P. 650)

The production of **olives** in the Cadiz district will be substantially the same as in 1920. The yield of olive oil will also be approximately the same as in 1920. (P. 651)

A decree recently issued by the Austrian government permits the importation of the following articles free of duty: **Coconut** and **palm oils, mineral oils,** and **lignite.** (Pp. 652–3)

By a decree of October 3, 1921, the duty of 1 cent per kilo shall be levied on **copper, bronze,** and **brass** when imported into Salvador in ingots as raw material for industrial purposes. (P. 654)

JAPANESE MINERAL PRODUCTION

Minerals	June 1920	June 1921	January–June 1920	January–June 1921
Gold, oz	18,000	21,000	126,000	124,000
Silver, oz	420,000	357,000	2,570,000	2,330,000
Copper, lbs	11,900,000	10,200,000	73,100,000	61,000,000
Iron, metric tons	4,870	3,100	34,000	18,400
Coal, metric tons	2,220,000	1,840,000	13,400,000	11,900,000
Petroleum, gal	7,040,000	7,480,000	44,400,000	45,100,000
Sulfur, metric tons	3,700	2,700	22,000	13,000

It is noted from these figures that Japan's production of **minerals** and **ores** during the first half of the current year decreased in all cases except that of petroleum, which registered a slight increase of 1.5 per cent, compared with the first six months of the preceding year. (P. 659)

A slight improvement in the Japanese **chemical market** is noted. (P. 660)

The production of **glycerol** in Japan and China's trade in it are described. (P. 660)

A New South Wales iron company has taken up large areas on the west coast of Tasmania, which contain deposits of high-grade **iron ore.** It is expected that at least 20,000 tons of iron ore monthly will be drawn from these deposits. (P. 661)

The **petroleum** industry at Baku is at a standstill as regards production, and refining is practically stopped from lack of soda and acid. (P. 663)

The corrected Mexican **mineral** statistics for the January–June 1921 period are as follows:

	Pounds
Gold	22,972
Silver	2,033,129
Copper	101,538,043
Lead	267,716,152
Zinc	31,665,104
Quicksilver	170,261
Antimony	3,466,475
Graphite	6,418,777
Tungsten	76,083
Tin	3,501
Arsenic	2,642,890
Manganese	1,848,849

(P. 666)

The following lists of Brazilian importers and dealers have been mimeographed and copies may be obtained from the Bureau of Foreign and Domestic Commerce:

Importers of chemicals and dyes
Importers of drugs
Importers and dealers in oils

(Pp. 667–8)

An English translation of two projects for **petroleum** legislation presented to the Argentine Republic by the President, September 23 and 25, 1919, and also a translation of the President's message of July 20, 1921, on the same subject, are on file at the Bureau of Foreign and Domestic Commerce. (P. 675)

A favorable market for American **paints** and **varnishes** is reported in South Africa. (P. 697)

Portugese East Africa also offers a market for **paints** and **varnishes.** (P. 697)

The **metal industries** of Finland are described and the report is accompanied by tables showing the imports and exports of metals and manufacture. (Pp. 699–702)

The discovery of a large deposit of high-grade **iron ore** on the shores of Lake Athabasca, Alberta, Canada, is reported. The ore is said to contain 64 per cent of metallic iron. (P. 702)

There is a large **radium** content in the uranium ore found at Jachymov, in Bohemia, near the frontiers of Saxony. Although the radium production in the United States is greater as to quantity, the ores of Jachymov are richer in quality. The known supply of radium in the Jachymov district will last for 20 yrs., at the present rate of production. There are several by-products of considerable importance. Uranium dyes are produced, eleven workmen being employed in the dye factory. (P. 726)

Mineral fertilizers are finding a growing market among the farmers and orchardists in southern Spain according to reports of the American consuls at Cadiz and Seville. A steady increase is noted, and 20,000 tons have been given as an estimate as the probable consumption this year in the Seville district alone. (P. 726)

A market for **copper sulfate** is reported in southern Italy. (P. 726)

An important meeting was recently held at Rome to discuss means of assisting the **sulfur** industry, which is at present undergoing a period of depression. There are 200,000 tons of sulfur unsold in Sicily. It has not been possible to find a market for it in competition with American sulfur, which is delivered in Europe at about 520 lire per ton. The meeting adjourned without having attained any results. (P. 727)

Reports from Buenos Aires state that the Argentine **oil market** is keenly competitive and it is advisable for any firm contemplating the establishment of an agency to send a thoroughly competent expert to study the whole oil situation. (P. 739)

A market for American **gasoline** is said to exist in Natal. (P. 778)

A copy of the new **petroleum** law for Ecuador may be examined at the Bureau of Foreign and Domestic Commerce. (P. 779)

French engineers are endeavoring to discover a substitute which may diminish to a certain degree the present dependence on German **coke.** The possibilities of the Saar-Lorraine coal for the manufacture of coke are being studied. (Pp. 780–1)

The Japanese **copper** industry seems to be in a tight place, and copper companies are now agitating for increased customs duties, which will save them from the disastrous effects of foreign competition. (P. 793)

The Japanese **chemical industries** are showing a willingness to combine with foreign concerns. The worst depression, however, is felt by the **dyestuff** manufacturers, who, unless something is done for them, are faced with the prospect of seeing German imports capture the entire market. (P. 793)

Practically the entire **zinc** and **lead** industry of Upper Silesia has passed to Poland. This industry is relatively very important, the output of raw zinc in Upper Silesia in 1912 having been 168,500 tons, which was five-eighths of the total production of Germany and more than one-sixth of the world production. (Pp. 798–9)

The governor of the Province of Jujuy has requested the Argentine Senate to take measures to protect the **metallurgical industry** recently established in the Provinces of Salta and Jujuy. (P. 802)

Paraguay offers a considerable source of supply of **palm oil** for the American market. (P. 803)

STATISTICS OF EXPORTS TO THE UNITED STATES

ITALY—(P. 650)
Olive oil
UNITED KINGDOM—(P. 728)
Salt, not table
Lead
Tin

CONSTANTINOPLE—(Pp. 661, 801)
Borate stone
Gum tragacanth
Attar of roses
Glue stock
Opium

BOOK REVIEWS

Engineering Instruments and Meters. By Edgar A. Griffiths. xxiv + 360 pp. D. Van Nostrand Co., New York, 1921. Price, $7.50.

The author limits himself to the measurement of the fundamental quantities of mechanical science; consequently instruments in the fields of electrical and chemical engineering are omitted. It would seem desirable for the author, in any future editions, to cover these fields also, thus making the subject matter as broad as the title.

The book consists of eight chapters, dealing with the measurement of length, screw threads, area, volume, velocity, force and masses, work, and temperature.

Chapter I includes an interesting historical account of length standards and their duplication. In addition to the description of the usual length gages there is a good description of Johanssen's block gages, whereby any standard of length between 0.2 inch and 10.0 inches in steps of 0.0001 inch may be obtained with the accuracy of ±0.00004 inch by means of a set of eighty-one blocks.

The chapter on the measurement of screw threads gives a well-developed account of the measurement and inspection of screw threads, especially by means of optical projection methods.

Of particular interest in the chapter on the measurement of area are the parts dealing with the accuracy of planimeters and the method of obtaining the mean ordinate for circular charts. No area measuring machines are described, such as are in use in this country, for the area measurement of hides. The chapter on the measurement of volume discusses such instruments as displacement meters, orifices, venturi meters and pitot tubes in a thorough manner, in the light of the comparatively recent English developments on the flow of fluids. The chapter also includes a section dealing with the usual types of steam flow meters, together with a section on the electrical measuring instruments, such as the Thomas. Usual and unique styles of depth gages are also described.

Chapter V gives a thorough account of all sorts of tachometers and speedometers, together with the methods for the measuring of train and aircraft velocity. Classifying pitot tubes, etc., as volume meters in the previous chapter and again as instruments for the measurement of velocity in this chapter makes the treatment somewhat scattered. Chapter VI, on the measurement of force and the comparison of masses presents a well worth while description of the variations in construction and shows how these variations affect the sensibility and durability of balances. The discussion of the measurement of work deals with indicators, their construction and errors, together with the construction and relative advantages of various types of dynamometers.

The final chapter is an abbreviated one on the measurement of temperature and is not up to the standard of the rest of the book. It contains a description of the usual types of thermometers and pyrometers. There is a lack of clearness and effectiveness in the treatment of pyrometry, since the author does not set forth clearly that the difference in temperature between a hot and cold junction of a pyrometer sets up an e. m. f., not a "current" proportional to the temperature difference. Errors in pyrometry and methods of correction, base metal couples other than iron-constantin, pyrometer construction, and protection tubes are inadequately discussed. Radiation pyrometry is overemphasized, as compared with the treatment of optical pyrometers.

Following each chapter is a complete and useful bibliography that will be highly useful to one particularly interested in any given type of meter. The index is very poor. For example, orifices, although adequately treated in the text, are not mentioned in the index. The index for Venturi tubes refer to their use in measuring aircraft speed, while the main development of these instruments in Chapter IV is not indexed at all.

This book covers, in a thorough and interesting way, an almost untouched field of utmost importance and will prove itself of value to engineers, constructors, and investigators whose equipment or problem requires the measurement of mechanical force.

R. T. Haslam

The Electric Furnace. By J. N. Pring. xii + 485 pp. Longmans, Green & Co., 1921. Price, $10.50 net.

This is one of the monographs on industrial chemistry edited by Thorpe, whose preface points out that the object is to elucidate principles rather than to give technical details. The author's preface terms it a "general technical discussion of the position and prospects of high temperature industrial chemistry." The last four words would be as apt a title as the one used, for the author does better in dealing with the chemistry of the electric furnace than with the electric furnace itself.

Without the side-excursions into chemistry, the book, aside from being more recent, would not be of great value to the reader possessing Stansfield's work of the same title, which it closely resembles. With them, it is the best book so far available for a chemist who wishes a general survey of the electric furnace field, or for a student starting the study of electric furnaces.

It is written from the English viewpoint and with special reference to British conditions. The contents cover a historical discussion; laboratory furnaces (especially pressure furnaces); current supply; transformers; measurement of high temperatures; calcium carbide; fixed nitrogen; iron smelting; electric steel; ferro-alloys; nonferrous melting; zinc, copper and tin smelting; SiC, Si, Al_2O_3, graphite, P, and CS_2; Northrup and Hering furnaces; Al, Na, and Ca; refractories; heat losses, electrodes and electrode holders; power expenditure; water power developments (including India, Burma, and Tasmania, as well as the Severn tidal power project), and steam power stations. The chapters on nitrogen fixation are perhaps the best. The one on "current supply" is excellent.

The book is commendably free from descriptions of obsolete and merely "paper and patent" furnaces, though a few of them are included. In general the greatest weakness is not what has been put in but what has been left out. Notwithstanding that 500 pages are filled with close-packed, concisely written information, the electric furnace field is not covered at all fully, nor is the information at all up to date, especially as to American practice. Some fairly recent developments are touched on, such as the high-frequency furnace, preheating the charge for a Snyder steel furnace, the Fulton zinc furnace, and cyanide from cyanamide.

But a book aiming to cover the electric furnace field certainly ought to include the Ajax-Wyatt brass furnace and the Soderberg self-baking electrode, on which one reference each appears in the bibliography, but no mention in the text. The reader would not guess from the book that magnesium and phosphoric acid are commercial electric furnace products. What little information is given on electric brass melting is three years old and very sketchy. Synthetic cast iron is mentioned, but none of the recent progress in electric gray iron and semisteel. Electric annealing and heat-treating furnaces are entirely ignored. The section on ferro-alloys is rather inadequate.

The reviewer's conclusion is that a second volume of equal size would be required to cover, even as concisely as has been the case with the material dealt with, that which has been omitted and which is of equal importance.

There is a certain lack of perspective about the book. It is hard to tell the relative importance of what the author describes. A student taking up electric furnaces for the first time would as likely as not assume that induction furnaces are of equal importance in electric steel practice with direct arc furnaces. If he reads the tables of the number of furnaces of different types installed, and is of a sufficiently inquiring turn of mind to wonder why the direct arc type is so preponderant in steel, he will not find much to clear up the question in the text.

Glaring errors are rare. One occurs in quoting a figure of 168 kw. hr. per metric ton for melting red brass in a Rennerfelt furnace. This figure was once published, but is incorrect and not claimed to-day by the makers of the furnace.

A book of this type has largely to be written with a pair of scissors, of course, and the author intimates as much in his preface. Such a compilation is useful, and on the whole, this is well done, though neither complete nor entirely up to date.

H. W. Gillett

Colorimetric Analysis. By F. D. Snell. viii + 150 pp. D. Van Nostrand Co., New York, 1921. Price, $2.00.

An independent work on this subject is a desirable addition to the analyst's reference library. Somewhat of a Cinderella among analytical methods, it actually underwent the destined transformation in the evolution of spectroscopy. In fact the standard work on colorimetric methods (G. and H. Krüss, "Kolorimetrik und Spektralanalyse," L. Voss, Hamburg, 1909, 2nd Ed.) dwells largely with the phases of instrumental development from colorimeter to spectrophotometer. This preoccupation with instruments and principles leaves plenty of room for a book of the present type.

The first three chapters cover: conditions of use of colorimetric methods, apparatus and methods of using it, and figuring of results. The differentiation of colorimetric methods into those used for speed, with more or less sacrifice of accuracy, and those used for precision in the determination of very small quantities is clearly stated. The chapter on apparatus is adequate, if not exhaustive; it might have been more critical, and in particular have given some space to Dehn's contentions[1] with regard to optical distribution factors. The discussion on figuring results would be improved by reference to graphic methods, particularly in cases where speed is fundamental.

The essence of the book, however, is in Chapters IV to XVII, which contain valuable compendium of methods for the determination of Fe, Cu, C (in steel), Pb, Bi, As, Al, Cr, Ni, Co, Mn, Zn, K, Mg, Au, Ti, Vd, Wo, F, Cl, P, Si, B, O, S, beside oxides and acids of nitrogen, sulfur, selenium, etc. Several alternative methods are described wherever possible. Individual points invite some criticism, *e. g.*, in the estimation of iron by thiocyanate, the addition of a small amount of potassium persulfate to a solution is recommended (p. 33) to keep the iron oxidized if it is desired to preserve a sample or standard for several days. The reviewer's experience is that persulfate rapidly oxidizes the thiocyanate radicle, and that the ferrocyanide method (p. 36) is definitely preferable. In regard to Atack's estimation of Al by alizarin S,[2] the reviewer and his collaborators have been disappointed with this sensitive and promising method, as it does not seem to possess the immunity from interference by calcium and phosphates which is claimed for it. For the estimation of phosphorus and phosphate, the method of Taylor and Miller, as modified by Bell and Doisy[3] should be mentioned. It consists in the reduction of phosphomolybdate by a hydroquinol developer, giving a blue color, and is very satisfactory.

The last two chapters on colorimetry proper (color of water, oils, dyes) and on nephelometry are very meager. The former suffers from the total lack of any discussion of the nature of color, its specification, and measurement as such. Nephelometry is dismissed with a reference to P. Kober's paper.[4] Since the subject matter is explicitly limited by title to colorimetric methods, no criticism can be made of this, but since photometric and nephelometric methods are so closely allied to the colorimetric ones it may be hoped that some time they will be discussed together. The author's omission of all but one or two applications of colorimetry to the estimation of organic substances is less comprehensible. Not only are there many older applications in food, drug, etc., analysis, *e. g.*, for alcohols, acids, aldehydes, phenols, alkaloids, but more recently the number of special colorimetric methods in biochemistry has been greatly increased. The increasing importance of colorimetric methods for hydrogen-ion determination also remains unnoticed.

Taking these limitations into account, it appears that the book is essentially one on inorganic colorimetric analysis for the practicing analytical chemist. As such, it fills a need in a way helpful to every chemist who has occasion to speed up analytical procedure.

The book is clearly printed on paper free from excessive gloss, and is illustrated with cuts of various colorimeters.

S. E. Sheppard

The Chemical and Metallographic Examination of Iron, Steel, and Brass. By Wm. T. Hall and R. S. Williams. xiii + 501 pp. McGraw-Hill Book Co., 1921. Price, $5.00.

A few years ago Hall and Williams translated Bauer and Deiss with some additions of their own. The present volume retains emphasis on the necessity for accurate sampling, and other good features of Bauer and Deiss, but covers metallographic examination in somewhat greater detail, and the analytical methods are brought up to date, especially by a chapter and bibliography on electrometric methods.

The book stands out from the general run of laboratory manuals and reference books, because it is written from a broad viewpoint. We have too many such books written by analysts. This one is written by chemists. The young chemist who studies it cannot avoid understanding that proper sampling to take account of segregation, the use of accurate analytical methods, and consideration of the microstructure, are all equally important steps in answering questions as to the quality of a metal or alloy.

The book is written in an orderly fashion, clearly printed on good paper, and well indexed. The authors first discuss the chemical principles underlying each method of analysis, so that the essential precautions and the interferences are understood before the details of the method are given. Four or five methods are given for most of the common elements found in modern steels, but the relative advantages of each method are so clearly stated that the reader can make an intelligent choice. The limits of accuracy to be expected are usually given for each method, and analytical figures on the same material by different methods are often included. Methods are given for C, Mn, P, Si, S, Cu, Cr, Fe, Ni, Mo, W, V, Al, As, Co, Ti, Zr, N, and O in steel. The methods for nonferrous alloys are less complete, but standard methods for common determinations of elements in bearing metal, brass, and bronze are given. The light aluminium alloys are not covered either in the chemical or metallographic sections.

Only minor criticisms occur to the reviewer. Since methods involving separation of ferric chloride by ether are numerous in the book, it would have been well to point out that one can make this separation with a beaker, a stirring rod and a siphon without having to use the Rothe shaking funnel and increase the volume of the solution by washing out the original beaker. Since methods for zirconium are included, it would have been well to point out that both zirconium and titanium interfere with evolution of sulfur even in an annealed sample, and that the cupferron method given for zirconium is often more applicable for titanium than the methods given under that element.

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[1] "Fallacies in Colorimetry," *J. Am. Chem. Soc.*, **39** (1917), 1392.

[2] *J. Soc. Chem. Ind.*, **34** (1915), 936.

[3] *J. Biol. Chem.*, **44** (1920), 55.

[4] This Journal, **10** (1915), 843.

"Peptonization" (p. 309) might better be peptization, in the interests of "economy and efficiency" in spelling and pronunciation.

The statement (p. 248) that in steel "oxygen is present chiefly as ferrous oxide dissolved in the crystals of ferrite" may be correct, but in view of the differences of opinion on this subject among metallurgists, the statement seems a bit positive.

The metallographic end of the book is a trifle sketchy and elementary compared with the chemical end, but covers the essentials clearly. The reviewer would prefer fuller references to the literature.

If you have an analyst in your laboratory whom you wish to have analyze whatever samples are handed to him without question as to history of the sample, or application of the analysis, don't let him use this book, for it might lead him to become a chemist instead of an analyst.

H. W. Gillett

Naval Stores—History, Production, Distribution, and Consumption. Compiled by Thomas Gamble. 286 pages. Review Publishing & Printing Co., Savannah, Ga., 1921. Price, $3.25, postpaid.

Certain industries require a special treatment and that given to the naval stores industry in this volume is extremely appropriate. The illustrations are profuse and there is a wealth of introductory historical matter that would compel the interest of the layman who might not know the meaning of the name on the title page; even the immortal Samuel Johnson has contributed his mite: "I remember I used to think tar dirty, but when I knew it to be only a preparation of the juice of the pine, I thought so no longer."

Every corner of the earth that grows a pine capable of producing naval stores has been ransacked. All phases of the industry, such as methods of production, marketing, standards, uses, statistics on production, exports and prices, and future sources of supply receive consideration. The chapters bearing on wood turpentine and rosin are especially valuable. This phase of the industry, after many vicissitudes, is on a sound basis and has the promise of an increasingly great future.

It is a striking fact that the first great improvement in the industry resulted through the introduction of the cup and gutter system in 1901 through the energy of Dr. Herty, and this step to-day remains the high-water mark of advancement. Another fine piece of work was performed by Miss Eloise Gerry of the Forest Service. A microscopical study of tapped trees showed clearly the nature of resin flow, and, aside from the investigations of Tschirch, furnished the first really scientific information on which a rational method of tapping could be based.

Not so many years ago turpentine was the valuable product, the rosin being frequently run to waste. To-day the condition is reversed. The chief use of turpentine continues to be in paints and varnishes, but many manufacturers consider that only enough is necessary to give their finished products a "smell." Rosin has highly desirable properties for certain soaps and is practically indispensable in the sizing of the cheaper grades of paper.

In the settlement of a new country it is difficult to decide how much waste is compatible with proper economic development. There is no question, however, but that the exploitation of our forests has gone beyond the bounds of reason, and that the future must receive serious consideration. So many futile predictions have been made regarding the approximate time at which the present stands of timber will cease to be the largest factor in naval stores production, that it is useless to hazard a guess; but the end is just as certain as it is indefinite. Consequently it is gratifying to know that steps have been taken to perpetuate the industry through the growing of long leaf and Cuban pines, the latter being particularly desirable from the standpoint of rapidity of growth and resin production.

Great credit is due Mr. Thomas Gamble. While he has refrained from calling it a "labor of love," it could hardly have been otherwise.

A. W. Schorger

The Silver Bromide Grain of Photographic Emulsions. By A. P. H. Trivelli and S. E. Sheppard. 143 pages. D. Van Nostrand Co., New York, 1921. Price, $2.50.

This is the first volume of a series of monographs on the theory of photography from the Research Laboratory of the Eastman Kodak Company. Each is intended to be complete in itself, and to include not only work done at the research laboratory of the company, but also that available in the literature of the subject. If the standard of the initial volume is maintained, the series will be invaluable to students of the science of photography.

Since the silver halide grains are of very small size and precipitated in a colloid medium, they have usually been treated simply as colloid aggregates. In the present volume, however, a detailed study is made of these grains. It is established that they are definitely crystalline and belong to the regular system, though of widely different final shapes. The questions of their alteration by mechanical strains and of the modification of the gelatin structure are discussed. A study of the course of development of the silver halide emulsion by ammonia leads to the conclusion that the process is primarily a recrystallization of the silver halide as a halide-ammonia complex on nuclei furnished by the visible photochemical image; the hypothesis of mechanical disintegration by light therefore becomes unnecessary. This is contrary to the widely urged hypothesis of Lüppo-Cramer.

The formation of grains in the emulsion is studied in the light of the dispersion theory of von Weimarn, according to which the grain-subdivision of the initial precipitate is determined by the concentration of the solutions and by other physical conditions. The changes of this "dispersity" are now found to be connected with changes in the content of adsorbed impurities present. Crystallization catalysis by nuclei is suggested as an explanation of some of the effects produced by the admixture of silver iodide and silver bromide in an emulsion.

A bibliography is appended, and there are many references to original papers. The study of the relation between the sizes of grains and their photographic properties is reserved for a future monograph.

L. Derr

Statistical Supplement to the Final Report of the Nitrogen Products Committee of the Ministry of Munitions. By J. A. Harker, O.B.E., D.S.C., F.R.S., Director of the Nitrogen Research Laboratory, Ministry of Munitions, London. 22 pages. H. M. Stationery Office, Imperial House, Kingsway, W. C. 2. Price, One Shilling.

The above pamphlet supplements the statistical data published in the Final Report of the Nitrogen Products Committee of the Ministry of Munitions early in 1920 and should be obtained and bound with that Report, which is one of the best compilations on nitrogen fixation and the world nitrogen situation that has been published in any language. The present pamphlet simply brings the statistics of the nitrogen industry as nearly up to date as possible and covers all phases of the industry, including Chile nitrate, nitric acid, by-product ammonia, and the synthetic nitrogen industry. As always, Dr. Harker's work has been done well.

Charles L. Parsons

NEW PUBLICATIONS

Agricultural Chemistry: Chimie Agricole. C. André. 3d edition. 3 Vol. 1213 pp. Price, 20fr. J.-B. Baillière & Fils, Paris.

Analytical Chemistry. Vol. I, Qualitative Analysis. F. P. Treadwell and William T. Hall. 5th English edition. 597 pp. Price, $4.50 net John Wiley & Sons, Inc., New York.

Atomic Theories. F. H. Loring. 218 pp. Price, 12s. 6d. Methuen & Co., London.

Biochemistry: A Manual of Selected Biochemical Methods—as Applied to Urine, Blood and Gastric Analysis. Frank P. Underhill. 232 pp. Illustrated. Price, $3.00 net. John Wiley & Sons, Inc., New York.

Catalogue of British Scientific and Technical Books. Prepared by a committee of the British Science Guild, London. 376 pp. Price, 10s. net.

Chemistry. G. H. J. Adlam. Price, 3s. 6d. James Thin, Edinburgh.

Coal: Practical Chemistry of Coal. A. F. Findley and R. Wiggington 140 pp. Price, 12s. 6d. Benn Brothers, Ltd., London.

Confectioners' Raw Materials; Their Sources, Modes of Preparation, Chemical Composition, the Chief Impurities and Adulterations, Their More Important Uses and Other Points of Interest. James Grant. 173 pp. Price, $3.00. Longmans, Green & Co., New York.

Explosives: Manufacture and Uses of Explosives. R. C. Farmer. 116 pp. Price, 2s. 6d. net. Sir Isaac Pitman & Sons, Ltd., London.

Explosives: Technical Records of Explosives Supply 1915–1918. No. 3. Sulfuric Acid Concentration. No. 4. The Theory and Practice of Acid Mixing. Ministry of Munitions and Department of Scientific and Industrial Research. Price, 12s. each. H M Stationery Office, London.

Flotation: A Manual of Flotation Processes. Arthur F. Taggart. 192 pp. Price, $3.00. John Wiley & Sons, Inc., New York.

Forensic Chemistry. A. Lucas. 258 pp. Price, $5.25 net Longmans, Green & Co., New York.

Graphical Analysis: A Textbook on Graphic Statics. William S. Wolfe. 374 pp. 713 illustrations. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

Hydraulique Générale et Appliquée. Denis Eydoux. (Encyclopédie du Génie Civil et des Travaux Publics.) 504 pp. Illustrated. Price, 50 fr. J.-B. Baillière & Fils, Paris.

Inorganic Chemistry: A Textbook of Inorganic Chemistry. A F. Holleman. 527 pp. Price, 19s. net. Chapman & Hall, London.

Laboratory Manual of General Chemistry. Harry N Holmes. 115 pp. Price, $1.60. The Macmillan Co., New York.

Medical Chemistry: Chemistry and Analysis of Drugs and Medicines. Henry C. Fuller. 1072 pp. Illustrated. Price, $10.00. John Wiley & Sons, Inc., New York.

Medical Chemistry: Précis de Chimie Médicale. Desgrez. 476 pp. Illustrated. Price, 25fr. J.-B. Baillière & Fils, Paris.

Metallurgical Plants: Nos Usines Métallurgiques Dévastées 1914–1918. Monographies de quelques Grandes Usines Métallurgiques Francaises Détruites par les Allemands. Introduction by Léon Guillet. 234 pp. Illustrated. Price, 25 fr. La Revue de Métallurgie, Paris.

Microbiologie Agricole. E Kayser. 4th edition. 2 vol. 715 pp. 98 figures. Price, 20fr. J.-B. Baillière & Fils, Paris.

Mineralogy: A Manual of Determinative Mineralogy. Charles H. Warren. 163 pp. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

The Mineral Industry. Vol. XXIX. 1920. Edited by G. A. Roush and Allison Butts. 938 pp. Illustrated. Price, $10.00. McGraw-Hill Book Co., Inc, New York.

Mining Physics and Chemistry. J. W. Whitaker. 268 pp. Price, 9s. Edward Arnold & Co., London.

Modern Gasworks Practice. Alwyne Meade. 2d edition. 815 pp. Price, 55s. net. Benn Brothers, Ltd., London.

Organic Chemistry: Résumé Analytique du Cours de Chimie Organique. Paul Cazeneuve and Albert Morel. 2d edition. 432 pp. Price, 25fr. J.-B. Baillière & Fils, Paris.

Organic Medicaments: Préparation des Médicaments Organiques. E. Fourneau. 350 pp. Illustrated. Price, 25fr. J.-B. Baillière & Fils, Paris.

Paint and Color Mixing. A Practical Handbook for Painters, Decorators, Paint Manufacturers, Artists, and All Who Have to Mix Colors. Arthur S. Jennings. 6th edition. 253 pp. Illustrated. Price, $5.00. D. Van Nostrand Co., New York.

Practical Refrigeration. Compiled by Editorial Staff of *Power*. 283 pp. Illustrated. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

Quantitative Analysis: A Course of Instruction in Quantitative Chemical Analysis for Beginning Students. George McPhail Smith. Revised edition. 218 pp. Price, $2.25. The Macmillan Co., New York.

Quantitative Analysis: An Introductory Course of Quantitative Chemical Analysis with Explanatory Notes. Henry P. Talbot. 6th edition, completely rewritten. 203 pp. Price, $2.25. The Macmillan Co., New York.

Radioactivity and Radioactive Substances. J. Chadwick. 111 pp. Price, 2s. 6d net Sir Isaac Pitman & Sons, Ltd., London.

Tanning: Practical Tanning: A Handbook of Modern Practice and Processes as Applied in the Manufacture of Leather and Allied Products. Allen Rogers. New edition, completely rewritten. 900 pp. 125 illustrations. Price, $10.00. Henry Carey Baird & Co., Inc., New York.

Textile Chemistry: Introduction to Textile Chemistry. H. Harper. 189 pp. Illustrated. Price, $1.25. The Macmillan Co., New York.

Vegetable Oils: Les Huiles Végétales. H. Jumelle. 495 pp. 125 figures. Price, 15fr. J.-B. Baillière & Fils, Paris.

Vitamine Manual: A Presentation of Essential Data about the New Food Factors. Walter H. Eddy. 121 pp. Price, $2.50. Williams & Wilkins Co., Baltimore.

RECENT JOURNAL ARTICLES

Bleaching of Cotton. J. Merritt Matthews. *Color Trade Journal*, Vol. 9 (1921), No. 5, pp. 172–76.

Chemical Elements of Living Matter. Ingo W. D. Hackh. *American Journal of Pharmacy*, Vol. 93 (1921), No. 11, pp. 745–56.

Dyes: Organic Acids for Printing and Dyeing. A. J. Hall. *Textile Colorist*, Vol. 43 (1921), No. 515, pp. 741–43.

Dyes: La Naphtaline au Point de Vue Scientifique et Industriel. M. E. Noelting. *Revue Générale des Matières Colorantes de la Teinture, de l'Impression et des Apprêts*, Vol. 26 (1921), No. 298, pp. 145–51.

Enamels: Some Relations of Composition to Solubility of Enamels in Acids. Homer F. Staley. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 9, pp. 703–17.

Glass: The Development of Various Types of Glass. Parts XII, XIII, XIV, XV, XVI. C. J. Peddle. *Journal of the Society of Glass Technology*, Vol. 5 (1921), No. 19, pp. 201–268.

Heat Balance in the Kier Boil. Paul A. Merriam. *American Dyestuff Reporter*, Vol. 9 (1921), No. 19, Sec. 2, pp. 13–18.

Leather: The Microscope as Applied in the Manufacture of Leather. Robin Bruce Croad and Fini G. A. Enna. *Journal of the American Leather Chemists Association*, Vol. 16 (1921), No. 12, pp. 690–95.

Leather: Recovery of Acetic Acid during the Evaporation of Tanning Extracts. Georges Vie. *Journal of the American Leather Chemists Association*, Vol. 16 (1921), No. 11, pp. 641–44. Translated from *Le Cuir*, 10 (1921), 329.

Naval Stores: The Manufacture of Naval Stores from the Dead Wood of the Southern Pines. C. M. Sherwood. *Chemical and Metallurgical Engineering*, Vol. 25 (1921), No. 22, pp. 994–98.

Oil: The Relation between Alcohol-Water Solubility and Spontaneous Ignition Temperatures. W. R. Ormandy and E. C. Craven. *Journal of the Institution of Petroleum Technologists*, Vol. 7 (1921), No. 28, pp. 325–34.

Photomicrographic Method for the Determination of Particle Size of Paint and Rubber Pigments. Henry Green. *Journal of the Franklin Institute*, Vol. 192 (1921), No. 5, pp. 637–66.

Polariscope as an Aid in the Identification of Alkaloids. A. G. Murray. *Journal of the American Pharmaceutical Association*, Vol. 10 (1921), No. 10, pp. 736–42.

Porcelain: Use of Special Oxides in Porcelain Bodies. R. F. Geller and B. J. Woods. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 10, pp. 842–54.

Potash: Les Gisements de Potasse d'Alsace et l'Etat de leur Exploitation. Camille Matignon. *Chimie et Industrie*, Vol. 6 (1921), No 4, pp. 440–64.

Rubber: The Discontinuity of Vulcanization in the Presence of Organic Accelerators. D. F. Twiss. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 20, pp. 242*t*–48*t*.

Rubber: The Problem of Solvent Recovery. P. Wilson Gumaer. *The Rubber Age*, Vol. 10 (1921), No. 3, pp. 85–87.

MARKET REPORT—DECEMBER, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Dec. 1	Dec. 15
Acid, Boric, cryst., bbls.	lb.	.12$^{3}/_{4}$	.12$^{3}/_{4}$
Hydrochloric, com'l, 20°	lb.	.01$^{1}/_{2}$	.01$^{1}/_{2}$
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.06$^{3}/_{4}$	.06$^{3}/_{4}$
Phosphoric, 50% tech	lb.	.12	.12
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	17.00	17.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb.	*.03$^{1}/_{2}$	*.03$^{3}/_{4}$
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	*.07$^{1}/_{2}$	*.07
Ammonia Water, carboys, 26°	lb.	.07$^{1}/_{2}$	.07$^{1}/_{2}$
Arsenic, white	lb.	.06	.05$^{1}/_{2}$
Barium Chloride	ton	*50.00	*50.00
Nitrate	lb.	*.07	*.07
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works,	100 lbs.	2.25	2.25
Borax, cryst., bbls	lb.	.05$^{3}/_{4}$	.05$^{3}/_{4}$
Bromine, pure	lb.	.20	.20
Calcium Chloride, fused, f. o. b. N. Y.	ton	28.75	28.75
Chalk, precipitated, light	lb.	.03$^{1}/_{2}$	03$^{1}/_{2}$
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.30	5.55
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.50	3.80
Lead Acetate, white crystals	lb.	.12	.12
Nitrate	lb.	.15	.15
Red American	100 lbs.	.08	.08
White American	100 lbs.	.06$^{1}/_{2}$	.06$^{1}/_{2}$
Lime Acetate	100 lbs.	1.75	1.75
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, tech	lb.	.06	.06
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*45.00	*52.00
Phosphorus, yellow	lb.	*.28	* 28
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.10$^{1}/_{2}$	.10$^{1}/_{2}$
Bromide, imported	lb.	*.14	*.14
Carbonate, calc., 80–85%	lb.	.04$^{1}/_{2}$	.04$^{1}/_{2}$
Chlorate, cryst	lb.	*.06	*.06
Hydroxide, 88–92%	lb.	*.05$^{1}/_{2}$	*.05$^{1}/_{2}$
Iodide, bulk	lb.	2.60	2.90
Nitrate	lb.	.08	.08
Permanganate, U. S. P.	lb.	*.16	*.15
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.45$^{1}/_{2}$	.44$^{1}/_{4}$
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	*2.00	*1.85
Caustic, 76%	100 lbs.	*3.90	*3.85
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.08	.08
Chlorate	lb.	.07$^{1}/_{2}$	.07$^{1}/_{2}$
Cyanide	lb.	*.27	*.27
Fluoride, technical	lb.	*.10	*.10
Hyposulfite, bbls	100 lbs.	3.50	3.50
Nitrate, 95%	100 lbs.	2.25	2.25
Silicate, 40°	lb.	.01$^{1}/_{2}$	.01$^{1}/_{2}$
Sulfide, 60% fused	lb.	*.04$^{1}/_{4}$	*.04$^{1}/_{4}$
Bisulfite, powdered	lb.	.04$^{1}/_{2}$	.04$^{1}/_{2}$
Strontium Nitrate	lb.	*.11	*.11
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride. 50% sol'n	lb.	.09$^{3}/_{4}$	.09$^{3}/_{4}$
Oxide	lb.	.38	.38
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.08	.08

ORGANIC CHEMICALS

		Dec. 1	Dec. 15
Acetanilide	lb.	*.29	*.29
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.10	.10
Acetylsalicylic	lb.	.65	.70
Benzoic, U. S. P., ex-toluene	lb.	.65	.60
Carbolic, cryst., U. S. P., drs.	lb.	.10	.10
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	*.45	*.44
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.14$^{1}/_{2}$	.14$^{1}/_{2}$
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.22	.24
Tartaric, crystals, U. S. P.	lb.	*.27	*.26
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12$^{1}/_{2}$	.12$^{1}/_{2}$
Alcohol, denatured, complete	gal.	.44	.46
Ethyl, 190 proof	gal.	4.85	4.85
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap, refined	lb.	.90	.90
Carbon Bisulfide	lb.	.06$^{1}/_{2}$	.06$^{1}/_{2}$
Tetrachloride	lb.	.10$^{1}/_{2}$	.10$^{1}/_{2}$
Chloroform, U. S. P.	lb.	*.36	*.36
Creosote, U. S. P.	lb.	.40	.40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.45	2.45
Imported Potato	lb.	.08$^{1}/_{2}$	.08$^{1}/_{2}$
Ether, U. S. P., conc., 100 lbs.	lb.	.14	.14
Formaldehyde	lb.	.10$^{1}/_{2}$	.10$^{1}/_{2}$
Glycerol, dynamite, drums	lb.	.12^{1}/	.14
Methanol, pure, bbls	gal.	.85	.85
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	1.88	1.88
Potato, Jap	lb.	.08	.08
Rice	lb.	.18	.18
Sago	lb.	.04	.04

OILS, WAXES, ETC.

		Dec. 1	Dec. 15
Beeswax, pure, white	lb.	.35	.33
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10$^{1}/_{2}$	.10$^{1}/_{2}$
Ceresin, yellow	lb.	.08	.07$^{1}/_{2}$
Corn Oil, crude, tanks, mills	lb.	.07$^{3}/_{4}$	.07$^{3}/_{4}$
Cottonseed Oil, crude, f. o. b. mill	lb.	.06$^{7}/_{8}$	.07
Linseed Oil, raw (car lots)	gal.	.67	.67
Menhaden Oil, crude (southern)	gal.	.33	.33
Neat's-foot Oil, 20°	gal.	1.25	1.25
Paraffin, 128–130 m. p., ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs	bbl.	5.60	5.40
Rosin Oil, first run	gal.	.35	.35
Shellac, T. N.	lb.	.65	.65
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.82	.82
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.80	.81

METALS

		Dec. 1	Dec. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.55	4.55
Bismuth	lb.	1.55	1.65
Copper, electrolytic	lb.	.13$^{5}/_{8}$	.13$^{7}/_{8}$
Lake	lb.	.13$^{1}/_{2}$	.13$^{3}/_{4}$
Lead, N. Y.	lb.	.04$^{3}/_{4}$	.04$^{3}/_{4}$
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	80.00	78.00
Quicksilver, flask	75 lbs. ea.	45.00	52.00
Silver, foreign	oz.	.66$^{1}/_{4}$	.65$^{3}/_{4}$
Tin	lb.	.30	.32
Tungsten Wolframite	per unit	2.50	2.50
Zinc, N. Y.	100 lbs.	5.10	5.25

FERTILIZER MATERIALS

		Dec. 1	Dec. 15
Ammonium Sulfate, export	100 lbs.	2.60	2.60
Blood, dried, f. o. b. N. Y.	unit	3.50	3.50
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works	unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.75	.75
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American maker's price).

COAL-TAR CHEMICALS

Crudes

		Dec. 1	Dec. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U. S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	.06$^{1}/_{2}$	.06$^{1}/_{2}$
Phenol, drums	lb.	.10	.10
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.45	.45

Intermediates

		Dec. 1	Dec. 15
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.25	2.25
H	lb.	1.00	1.00
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.40	2.40
Naphthionic, crude	lb.	.65	.65
Nevile & Winther's	lb.	1.35	1.30
Phthalic	lb.	.40	.38
Picric	lb.	.30	.30
Sulfanilic	lb.	.27	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.17$^{1}/_{2}$	17
Aniline Salt	lb.	.26	.26
Anthraquinone	lb.	1.50	1.50
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.25	1.25
Benzidine (Base)	lb.	1.00	.90
Benzidine Sulfate	lb.	.75	.70
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.10	1.00
Dimethylaniline	lb.	.42	.40
Dinitrobenzene	lb.	.21	.21
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.60
G Salt	lb.	.70	.70
Hydroquinol	lb.	.90	1.35
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.10	.10
Monoethylaniline	lb.	1.00	1.00
a-Naphthylamine	lb.	.30	.30
b-Naphthylamine (Sublimed)	lb.	1.50	1.50
b-Naphthol, dist.	lb.	.30	.30
m-Nitroaniline	lb.	.85	.85
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	.11$^{1}/_{2}$	.11$^{1}/_{2}$
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	—	—
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.70	.70
m-Phenylenediamine	lb.	1.10	1.10
p-Phenylenediamine	lb.	1.70	1.60
Phthalic Anhydride	lb.	.38	.38
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	2.00	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.40	.40
Tolidine (Base)	lb.	1.20	1.20
Toluidine, mixed	lb.	.30	.30
o-Toluidine	lb.	.20	.20
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.10	1.10
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Dec. 1	Dec. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50

Acid Colors *(Concluded)*

		Dec. 1	Dec. 15
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Alkali Blue, domestic	lb.	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	7.50	7.50
Indigotin, conc.	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Dec. 1	Dec. 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc.	lb.	1.10	1.10
Chrysophenine, domestic	lb.	1.10	1.10
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Dec. 1	Dec. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Dec. 1	Dec. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.75	.75

Chrome Colors

		Dec. 1	Dec. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.65	.65
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Dec. 1	Dec. 15
Auramine, O, domestic	lb.	1.80	1.80
Auramine, OO	lb.	3.00	3.00
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	2.25	2.25
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc	lb.	8.50	8.50
Victoria Blue, base, domestic	lb.	5.40	5.40
Victoria Green	lb.	2.00	2.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of
INDUSTRIAL & ENGINEERING CHEMISTRY
Published Monthly by The American Chemical Society

Editor: H. E. Howe
Assistant to the Editor: N. A. Parkinson
Associate Editor: Wilkinson Stark (One Madison Ave., New York City)

Advisory Board: H. E. Barnard, J. W. Beckman, A. D. Little, A. V. H. Mory, Chas. L. Reese, Geo. D. Rosengarten, T. B. Wagner

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Washington, D. C.
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Cable Address: JIECHEM (Washington)

Advertising Department:
170 Metropolitan Tower
New York City
Telephone: Gramercy 2145

Volume 14 FEBRUARY 1, 1922 No. 2

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Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, $1.00, Canada, Cuba and Mexico excepted.
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EDITORIALS

Our Unemployment Problem

No profession or class is free from the ill effects of such extensive unemployment as has occurred in the last year, but fate seems to have dealt in a particularly unkind fashion with the chemist. It has been something of a shock, after all of our efforts to have industry understand and appreciate what the chemist has done, to find him given so little consideration and in many cases among the very first to be dismissed with the approach of business curtailment.

The situation presents one of our principal tasks for the future. We cannot create new places for our unemployed chemists directly by such plans as have been proposed for the reduction of unemployment. The business before us is to convince the average business man that he can far better afford to dispense with nearly any other department than to close his research and control laboratories.

It is obvious that the chemists themselves must aid in such a campaign. Indeed, they must do the work. THIS JOURNAL will endeavor to assist them in every possible way. We shall henceforth devote space each month, under the heading "The Earning Power of Research," to the recital of instances where genuine scientific research conducted in educational institution or plant has proved of real commercial value, and more than justified the expense involved. We realize that much that will be offered will contain nothing new for many of our readers. We know, however, that a specialist in one field frequently knows little of what his neighbor is doing; so we urge readers to send us in detail examples from their own experience and reading which will enable our fellow chemists to recommend scientific research and laboratory control to their executives, on the basis of past performance and future promise. THIS JOURNAL, on its part, will endeavor to supply information on topics of current chemical interest, for the same purpose.

We chemists need someone to pray for us as did a pastor for a revivalist. He said, "Brother Jones, before you begins this discourse, there are some powerful bad negroes in this here congregation, and I want to pray for you," which he did in this fashion: "O Lord, give Brother Jones the eye of the eagle, that he may see sin from afar. Glue his ear to the gospel telephone, and connect him with the central skies. Illuminate his brow with a brightness that will make the fires of hell look like a tallow candle. Nail his hands to the gospel plough, and bow his head in some lonesome valley where prayer is much wanted to be said, and anoint him all over with the kerosene oil of Thy salvation and set him afire."

The War on Chemical Warfare

Neither the chemist nor the chemical manufacturer introduced chemical warfare to our Government. Our country called upon the scientists to provide new means of defense and adequate means of offense to cope with the enemy. The chemists one and all responded. The result is a matter of history. Notwithstanding the facts presented and supported by ample data to prove the humaneness, efficiency, and comparatively low cost of being prepared to defend ourselves by chemical methods approved and adopted by other nations, a popular sentimental feeling against chemical warfare has been aroused in our country by factors which we do not yet fully understand. The carefully considered recommendations of the committee of experts, of which the President of our Society was chairman, were disregarded. Submarines and aircraft were treated gently as compared with chemical warfare, it being admitted that neither of these devices could be controlled at this time by agreement, and that their development is more easily followed than chemical warfare, which can be perfected without publicity.

On the 7th of January the Committee on Limitation of Armament passed the following resolutions:

> The use in war of asphyxiating, poisonous or other gases and all analogous liquids, materials or devices, having been justly condemned by the general opinion of the civilized world and a prohibition of such use having been declared in treaties to which a majority of the civilized powers are parties:
>
> Now to the end that this prohibition shall be universally accepted as a part of international law binding alike the conscience and practice of nations, the signatory powers declare their assent to such prohibition, agree to be bound thereby between themselves and invite all other civilized nations to adhere thereto.

These resolutions brought out some illuminating discussions in which Mr. Sarraut and Mr. Balfour spoke at length. While these gentlemen supported the resolutions, their remarks seemed to make it clear that they could see nothing harmful in the effort to discourage chemical warfare by agreement, but that, after all, the time has not come when research with defense as the main objective can be discontinued. The proposals made by the resolutions simply reaffirm admitted principles of international law and a mere confirmation of the law without adding any sanctions to it cannot relieve the nations from taking precautions against those who are prepared to break the law and who might easily dominate the world by their indifference to law.

Mr. Balfour pointed out the fact which has been emphasized as well by the Committee of the League of Nations at Geneva, that it is perfectly impossible to prevent a nation bent upon this method of warfare from making its preparations in time of peace, no matter what the rules of war may be. No nation, therefore, can forego the duty of examining how such attacks can be effectively met.

It seems to us that in undertaking to set a laudable example to the rest of the world in matters of so-called humane warfare, we are in no way relieved of the necessity of continuing scientific research to the end that we may at least obtain for ourselves that advanced knowledge which is undoubtedly our greatest defense. The research chemist, unlike the militarist, is not impelled by a desire to test his discoveries in the field. He has other ways of determining their efficiency, and many of them will find commercial application.

It seems unfortunate that we are to be denied the assistance of nontoxic materials such as harmless lachrymators and smokes which may save life when employed for defense. If applied literally, the resolutions may debar high explosives which give rise to large amounts of carbon monoxide. The effects of this gas may easily lead to charges of gas warfare by an enemy anxious for such an excuse for retaliation in order to employ super-gas developed in secret.

However the resolutions may be interpreted by those holding different views on chemical warfare, we urge chemists to seize every opportunity to make the general public realize the position of research in the whole problem and the necessity for its continuance upon an adequate scale.

To us, the endeavor to abolish chemical warfare throughout the world by the resolutions of the present conference reminds us of the experience of King Canute in commanding the tides not to rise.

Criticism from Germany

A review of Whitmore's monograph on "Organic Mercury Compounds" was published in No. 43, p. 443 (1921) of *Apotheker Zeitung.* At the close of the review the author, F. Dietze, says:

> That American chemists should desire to create a literature of their own, independent of other countries, is easily understood. From different signs one can conclude, however, that this is to be done almost exclusively at the cost of German science and German industry. That the whole undertaking is in its foundation directed against Germany follows from the fact that the "Interallied Conference" has been godfather of the plan. The war which was ended three years ago is to be carried further in scientific and industrial lines! In view of this, one cannot welcome the publication of these monographs.

During the last half of the nineteenth century such men as J. P. Cooke, S. W. Johnson, Wolcott Gibbs, Nef, and many others still living, received their training and inspiration to research in chemistry in German laboratories. These men organized instruction and research in America after models they had seen in Germany. We owe to Germany a debt for this inspiration to research, which must never be forgotten. There is some need to recall this at a time when, because of Germany's glaring faults in other directions, some are inclined to belittle and condemn everything that Germany has done. I have no apology to make for Germany's bad faith and wrong aims in the conduct of the war, but we must be on our guard against some Americans who wish to copy her faults rather than her virtues.

American students contributed a not insignificant amount to the experimental researches which gave Germany such preëminence in chemistry at the beginning of the twentieth century. Some American chemists thought they could secure a better audience for their papers if these were published in German and this, to superficial observers, contributed still further to the apparent volume of chemical achievements in Germany. From 1880 onward, however, a steadily increasing number of American students were trained at home and the demand for chemists, both for teaching and for the industries, has been such that at the beginning of the war there were nearly half as many chemists in America as in Germany. From the statistics available, there were less than one-fifth as many in England and less than one-tenth as many in France as there were in Germany.

Under the conditions which obtained at the beginning of the twentieth century it is not surprising that some German chemists assumed the attitude that chemistry was a German science and that researches not published in German could be ignored. To Americans such an attitude is very closely related to the attempt of Germany's political leaders to impose German imperialism on other countries by force. Any similar spirit on the part of Englishmen, Frenchmen or Americans, either in the political field or in science, is just as intolerable as it was in Germans.

If the determination of Americans that we shall do our full share, in friendly coöperation with other countries, in the development of chemistry, and that we shall win recognition on the basis of the genuine value of our research work and of our publications, is considered in Germany as "a continuation of the war in the scientific domain" we must acknowledge that it is our intention to do this. But German chemists will find no chemists in the world more ready than Americans to coöperate with them in a spirit of friendly rivalry for the promotion of chemical science, provided only that they will meet us in the same spirit.

William A. Noyes
Editor, Scientific Series,
A. C. S. Monograph

Teach Appreciation

For some time we chemists have been telling each other how little our science is appreciated and we have found it both profitable and necessary to use various means for popularizing chemistry. The A. C. S. News Service has been invaluable. Books like "Creative Chemistry" have done great service, and there have been feature stories, popular lectures, etc. The results have fully justified the efforts, but have we begun at the right place?

It seems to us that little real progress has been made in teaching chemistry to those who may never become chemists. Potential doctors, lawyers, merchants, and chiefs are given the same courses in beginning and general chemistry as are the men who have years of chemistry definitely before them. Might we not do well to begin, even in high school, by teaching chemistry as a series of practical problems, so that an interest in the application of the science might be kindled and developed before the disjointed courses in general chemistry are started? Would it not be well also to offer chemical courses in our colleges and universities designed primarily to teach appreciation for what chemistry means, what it has done, and what it may do? We cannot prepare all men to become chemists, but it is highly important that all men have a sympathetic understanding of the subject, so that the trained chemist may be received as a professional man and given a professional man's opportunity.

There is ample material to-day from which to build lecture courses popular in nature and well illustrated, which will interest any group of people in industrial chemistry and the fundamental science upon which it rests. These courses would encourage the embryonic chemist in his own work and could be made to serve to emphasize the necessity for real fundamental research. They would certainly bring to many who can devote but an hour or two a week to the subject a real appreciation of chemistry and help to acquaint those who are to become engineers, financiers, and business men with the field occupied by the chemist and the relation of his work to theirs. Then, indeed, the chemist will step into his proper place, and when soft times pass he will not be summarily dismissed along with the plumber's helper. Who will make this interesting experiment in pedagogy?

An Example

A short time ago there appeared at one of our universities a dealer in scientific apparatus who urged importation, and in stressing his capabilities as an importer claimed that he was buying for all the Jesuit colleges of the United States, importing their needs from foreign sources.

The position of This Journal has frequently been stated, namely, that so long as the manufacturers of American scientific apparatus and supplies deal fairly with educational institutions, we shall vigorously support the policy of buying only American-made equipment from American firms. Consequently we wanted to know how correct the importer's statement might be, and we corresponded with one of the councilors of the Society who is in a position to determine what is taking place. As a result of his activity, questionnaires were returned to him from 41 colleges and institutions with the unanimous statement that they are committed to the exclusive purchase of American-made apparatus and supplies in so far as their needs can be met. The personal letters received with the questionnaires breathe an admirable spirit of loyalty and patriotism. It would be interesting to know to what extent the excellent example set by the Jesuit institutions is being followed at our other seats of learning.

The Earning Power of Research

There is at least one textile mill in America which has continued to run at capacity. It has experienced no season of slack orders and it has made no reduction in its scientific staff. The president of this mill—Joseph Bancroft & Sons Co.—tells us that this success has been due to the fact that his scientists by continued research have kept his mill four or five years ahead of the procession. He is producing materials that have no competition. He is offering uniquely dyed fabrics which are in a class by themselves and when there is a buyers' market, a mill in this position has an unusual advantage. The president of this mill proposes to increase research, for he knows he cannot possibly afford to curtail it.

—

The world's largest producer of sulfite pulp, the Brown Corporation, installed a research and control laboratory some years ago, after the chemical engineer, who now is director of research as well, had demonstrated the utility of science in the establishment. This manufacturer has been quick to realize that in research he holds two trump cards. First, he is able to produce such good pulp that in a buyers' market his product is preferred. Second, he has been able to reduce his costs so that he has an advantage in competition, and at the same time he has so increased his quality as to be granted a premium on nearly all markets. The research staff of this mill has been steadily enlarged and strengthened and year by year has been responsible for the creation of new industries based upon the utilization of by-products to an extent where they rival in commercial importance the industry which was formerly the sole activity of the establishment.

— — —

Only a few years ago the rare elements occurring in the atmosphere were merely laboratory curiosities for which no one dreamed of industrial application. One by one these elements have found their place in commerce and now after some months of intensive research neon appears as a bread winner. Ignition gages have been devised in which purified neon is used in a tube which glows when brought into contact with spark plugs and other points where current is passing. The Air Reduction Company has developed a gage in which there are no wires, while the Westinghouse Company has used neon in a Geissler-like tube for a similar purpose. Beginning with the use of this gage in detecting ignition troubles in gas engines, it now appears that the field of usefulness is much wider. The discovery of static charges around factories where inflammable vapors are present, or on fire doors, belting, and machinery which is not properly grounded suggests possible applications. The neon tube glows when applied to the outside insulation of wires carrying over 2000 volts. It will be seen that the number of applications means a large number of such gages, and there is no doubt that research in this instance will return a large percentage on the investment.

Business Men Speak

The 1420 constituent organizations of the Chamber of Commerce of the United States have just voted upon a referendum submitted by the Committee on Tariff Principles. By a vote of $1840^{1}/_{2}$ to $27^{1}/_{2}$ the Chamber of Commerce is committed in favor of reasonable protection for American industries subject to destructive competition from abroad and of benefit to any considerable section of the country, $1846^{1}/_{2}$ to $37^{1}/_{2}$ in favor of maintaining in principle the anti-dumping legislation of May 1921, and by 1868 to 26 for tariff legislation framed and administered with a view to meeting discriminations direct or indirect by other countries against American trade. By a vote of $1793^{1}/_{2}$ to $59^{1}/_{2}$ the Chamber of Commerce recommends that the principle of maintenance and encouragement of our export trade should be observed in tariff legislation so far as consistent with reasonable protection for American industries of benefit to any considerable section of the country and subject to destructive competition from abroad.

In the Chamber an organization has one vote for the first 25 members, an additional vote for each 200, but no organization, however large, can have more than ten votes. It is obvious, therefore, that this vote represents the business men of the country and even Congress can hardly fail to take notice of the demand for the prompt enactment of suitable tariff legislation.

The Technical Press

It is a privilege to publish in this issue the excellent paper on "The Technical Magazine and Its New Relation to Industry," by H. C. Parmelee. We like the presentation, applaud the high standard of ethics set up for the modern technical paper, and agree with most of the conclusions reached by the author.

At the same time, we wish to make our own position clear, since we do not experience the editorial restrictions in This Journal which the author stresses in the fourth paragraph under "The Functions of the Technical Paper." It may easily be that editors of other scientific society magazines are less fortunate than we are, but with our Committee on National Policy empowered to act for the Society, official opinions can be had whenever they are necessary. There is neither delay nor difficulty in obtaining action, and when we do speak for the Society a message goes forth with the full strength of the world's largest scientific body.

Fortunately also the interests of our individual members, our Society, and the industry which we serve are identical. Our members and readers represent the industry, and it might almost be said that they are stockholders directly concerned in the success of This Journal and the extension of its influence.

The support of our strong Society gives us confidence and courage to undertake many a campaign and to strike out into new fields to advance science and industry. We welcome an opportunity to unite with *Chemical and Metallurgical Engineering* and with other modern technical papers in the distribution of authoritative and constructive news, in a manner satisfactory to the scientist and public alike.

Reinforcements

Burt P. Garnett has been appointed to succeed John Walker Harrington as Technical Manager of the A. C. S. News Service, Mr. Harrington having left the Service January 1 after a service which places us under many obligations. Mr. Garnett comes to us with extensive experience in newspaper work, in publicity, and other lines which well qualify him to carry on this important activity of the Society.

Wilkinson Stark has been appointed Associate Editor with offices at One Madison Avenue, New York City. He has had extensive laboratory and plant experience and will represent the Journal in the field. When he calls upon you, give him your best coöperation and keep him informed as to events in the field of industrial chemistry, new processes, and research.

Dr. R. P. Fischelis, who has been a member of this staff for the past year in the capacity of special writer, will continue in the same capacity.

ORIGINAL PAPERS

Electric Heat for Thermal Processes[1]

By E. F. Collins[2]

General Electric Co., Schenectady, New York

Heat energy application in this country has been largely the composite result of promotion and advertisement rather than of engineering. We have had fuel oil advocates, gas burning experts, powdered coal enthusiasts, fuel oil specialists, etc., but have, until recently, lacked the competent furnace engineer familiar with all types of furnaces, who could sit as court of appeal and give unbiased decisions regarding the true economic value of various heat sources for a specific work. To operate with gas a process that might much more advantageously be carried out with other forms of energy is not economy, yet many such cases exist to-day.

Fig. 1 shows the relative costs of four common sources of heat, *viz.*, coal, gas, fuel oil, and electricity, in terms of dollars per 100,000 B. t. u. utilized in baking ovens and furnaces. This chart in itself is evidence of the fact that considerations other than B. t. u. cost determine the true efficiency of thermal processes. For, were this not true, how could the electric furnace exist, and how could it show the greater over-all economy that it does in many processes to-day? Neither could the other two fuels compete with bituminous coal, did not the application of fuel oil or gas carry with it inherent advantages that completely outweighed the difference in cost of the B. t. u. supply. This is the true reason for the use of oil and gas rather than bituminous coal for many thermal processes. For the same reason electric heat is to-day recognized by competent engineers as the "last word" in carrying through many thermal processes with maximum safety, uniformity, and economy.

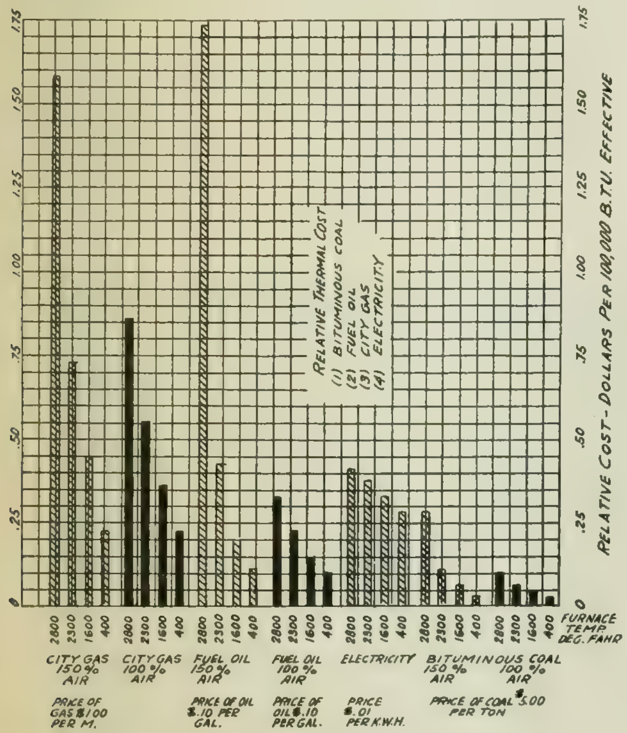

Fig. 1

It is a matter of no distant time when the use of electric heat for important thermal processes will be adopted with no more hesitation than now occurs when the householder decides in favor of the electric light instead of the gas lamp for his home, even though the cost of current consumed be greater than the cost of the gas.

Fig. 1 also illustrates well a valuable characteristic of electric heat. It will be noted that the cost of burning fuels varies widely, depending upon the amount of air admitted to furnace and the resultant combustion, *e. g.*, the cost of city gas for 100,000 B. t. u. effective rises to double its value with an increase of 50 per cent in air, and such excess percentage of air is by no means rare. Fuel oil likewise increases its cost roughly four times at the same temperature (2800° F.) and the same excess of air (50 per cent). Thus it is seen to how great an extent the economic operation of the fuel furnace is in the hands of the operator. This handicap does not exist with the electric furnace, where the ratio of conversion from power to heat is 100 per cent perfect and the operator cannot affect this efficiency of conversion.

FEATURES OF ELECTRIC HEATING

Some of the more important features of electric heating which distinguish it from fuel-fired equipment are the following:

HEAT GENERATION

1—Released at points to give uniform or nonuniform temperature.
2—Heat generation balanced against heat absorption.
3—Heat generated at or near potential of heating chamber.
4—Generated in inactive or dead atmosphere—no contamination of charge. Heating chamber may be a vacuum or under heavy pressure. Artificial atmosphere possible, as hydrogen gas, nitrogen gas, and no combustion gases.

HEAT CONSERVATION RESULTING IN HIGH THERMAL EFFICIENCY

1—High heat lagging, no local high temperatures.
2—Small heating chamber and no combustion chamber.
3—No hot gases leaving furnace, save for ventilation (when necessary).
4—Automatic control of temperature so that supply balances demand.

METHOD OF ELECTRIC HEAT TRANSMISSION AND DELIVERY TO CHARGE

1—Convection of liquids and gases (natural).
2—Circulation of liquids and gases (forced).
3—Radiation and convection in air.
4—Direct radiation to work.
5—Direct and reflected radiation to work.
6—Heat generated directly in charge by current flowing through it.
7—Complete heat saturation of charge without surface overheating, due to perfect automatic heat control.

HEAT GENERATION

In the electric furnace, heat generation can be kept nicely balanced against heat adsorption by the charge. The importance of this fact cannot be overemphasized, since the problem of heat absorption is of first importance in all heating and, especially, combustion furnaces. It goes without saying that efficient generation or development of heat units by chemical oxidation means little, unless the B. t. u. released are in a minimum constant proportion to the B. t. u. absorbed in doing useful work. Hence the rate of heat generation and heat absorption must be skilfully controlled to guarantee maximum over-all efficiency. To burn fuel correctly is therefore only the first step that has an immediate bearing upon practical results. This very fundamental truth should be recognized by all furnace users.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Consulting Engineer in Industrial Heating, General Electric Co.

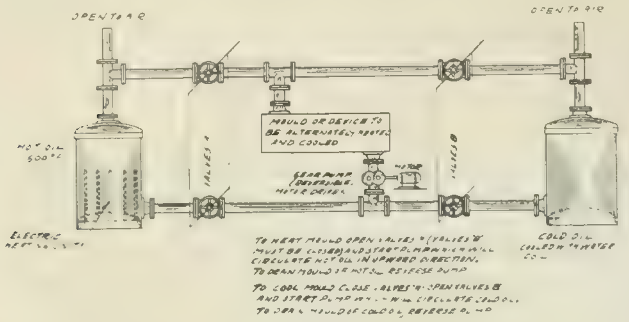
OPEN TO AIR
OPEN TO AIR
MOULD OR DEVICE TO BE ALTERNATELY HEATED AND COOLED
HOT OIL 500°F
VALVES A
VALVES B
GEAR PUMP (REVERSIBLE) MOTOR DRIVEN
MOTOR
ELECTRIC HEAT UNITS
COLD OIL COOLED WITH WATER COIL
TO HEAT MOULD OPEN VALVES A (VALVES B MUST BE CLOSED) AND START PUMP WHICH WILL CIRCULATE HOT OIL IN UPWARD DIRECTION.
TO DRAIN MOULD OF HOT OIL REVERSE PUMP
TO COOL MOULD CLOSE VALVES A OPEN VALVES B AND START PUMP WHICH WILL CIRCULATE COLD OIL.
TO DRAIN MOULD OF COLD OIL REVERSE PUMP

Fig. 2

Heat Transmission to Charge

Heat is transmitted by three means, *viz.*, (1) convection in liquids or gases, (2) conduction in liquids or solids, and (3) radiation through space or the ether.

When nonuniform heating occurs at different points in a fluid, uniformity of heating may or may not be established as a result of convection currents set up by difference in specific gravity resulting from the difference in temperature. Thus heat itself may establish and furnish the motive power for propelling currents of fluid, which in turn carry and distribute heat throughout the body of the fluid, or other forces may act to set the fluid in motion and thus distribute the heat. In the first case, gravity determines the direction of currents, whereas, in the second, currents may be made to travel more or less as desired. In general, uniformity of heating by convection is made more sure by the second method or by continuous agitation of the fluid, usually mechanical.

If the fluid be the product of combustion, as in a fuel fired furnace, consisting largely of carbon dioxide, water vapor, and nitrogen, currents and eddies exist in the combustion chamber owing to changes in densities depending in part on variation in temperature. These gases have a continuous flow, and practical results are obtained by removing as much heat as possible from such streams while they are passing through the furnace to the stack. Complete and properly regulated envelopment of the charge by the hot gases is necessary to a uniform and high rate of heat absorption, which is dependent upon the heat conductivity of the charge and the area of surface contact. If only parts of the body lie in the stream or if the streams vary in velocity or temperature, nonuniform heating may be expected. It should be remembered that in fuel fired furnaces, especially where forced draught is used, these currents of hot gases have a cyclonic violence and continuously shift as erratically.

CONVECTED VERSUS RADIANT HEAT—Convected heat is deposited at the surface of the body being heated. If the body is a solid, this heat must penetrate it by thermal conduction. Radiant heat, such as may be employed in the electric furnace, has a penetrating characteristic that enables it to pass directly into the charge more or less without being deposited on the surface. This results in a more rapid heating and a better or more complete penetration or distribution through the charge without excessive surface heating.

Importance of Heat Insulation

Heat must flow into or through a solid against a certain resistance which is called "the thermal resistance" of the body. As in electricity we call low resistance materials conductors and high resistance materials insulators, so in the thermal circuit we call materials of low thermal ohms per unit length and cross section "conductors of heat," while those of high thermal ohms per unit length and cross section are known as "insulators of heat" or "thermal insulators." Some heat insulators may be injured by low temperatures; others may be subjected to high temperatures without injury, mechanical or otherwise. The latter class are usually called "heat insulating refractories." Certain refractory materials are also exceptionally good heat conductors. Many good refractories at moderate temperatures become relatively good heat conductors when heated to a considerably higher temperature. In other words, they possess a high thermal resistance when cold and a very low thermal resistance when hot. Hence the furnace designer must select proper heat insulating materials.

Knowing definitely the thermal resistance of refractories and heat insulators, we may calculate the heat which will flow into or through such material under any assumed difference in temperature or thermal potential, as follows:

$$\text{Heat quantity in B. t. u.} = \frac{\text{Thermal potential difference}}{\text{Thermal ohms}}$$

Such a method allows the selection of proper materials and the proper combination to form a simple or composite furnace wall construction suited to withstand desired temperatures with a heat leakage through the walls which may be calculated with all the accuracy that practical considerations require.

This insulation of heat becomes important in the electric furnace because with *high heat insulation and perfect conversion of heat*, the stand-by loss becomes a fixed minimum for any temperature and constantly corresponds to a definite input of electric power, independent of the operator. Hence the performance of the electric furnace may be definitely predicted very accurately for any load. Owing to the variable combustion efficiency of the fuel fired furnace (Fig. 1), uniform performance and thermal efficiency is at the mercy of the furnace operator, the fuel, and the air supply.

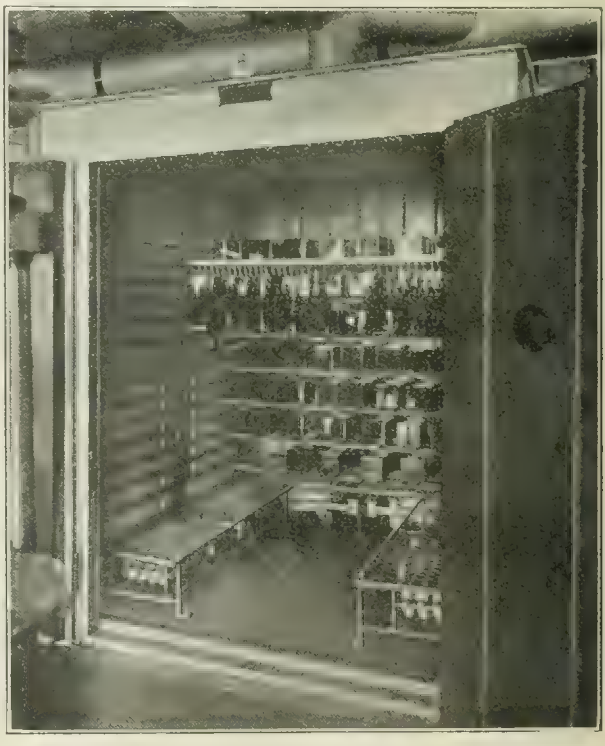

Fig. 3

APPLICATIONS OF ELECTRIC HEAT

Many successful working installations of electric heat exist to-day, and it is predicted that many more industrial processes will be improved and made more economically productive by the application of electrically generated heat. A few of the many such installations are illustrated herewith.

Fig. 2 shows a design for the application of electric heat to hot plates, hot presses, molds, vulcanizers, etc., which require alternate heating and cooling. The system is very simple and has a partial regenerative character, returning all heated oil to the tank before cooling the mold; thus it tends to require less cooling water in addition to affording a saving of heat. This arrangement has a higher inherent thermal efficiency, especially at high temperatures, than if heated and cooled alternately by steam and water.

Fig. 3 is a japan baking oven for telephone instrument parts. This oven is equipped with 18 kw. of heaters, and its dimensions are 7 ft. 10 in. high, 6 ft. wide, and 6 ft. 3 in. deep.

Fig. 4 shows one of a battery of ovens in use for making automobile engine cores. Core weights vary from 3 to 128 lbs. each. A very heavy linseed oil binder is used which makes it necessary to provide ventilation, and hence heat in excess of the requirements of the ordinary core compounds. The inside dimensions of the oven are 5 ft. wide, 10 ft. deep, and 7 ft. high. The connected load in heaters is 86 kw. Automatic temperature control is used. A baking temperature of 425° F. is used, which reduces the baking time from 1 to 3 hrs. over that required by the gas oven operating at 350°, the highest practical baking temperature with gas heating. Four of these ovens work at efficiencies varying from 10.9 to 14.6 lbs. of green cores baked per kw. hr. of power consumed. The total cores baked in four ovens for 1 wk. were 108,730 lbs., and the power consumption corresponded to 9389 kw. hrs., giving an efficiency of 11.6 lbs. of cores per kw. hr. During a year period, these ovens did not turn out a car of burned, cracked, or imperfectly baked cores.

Electric heat makes a highly efficient protective zinc coating possible by the sherardizing process. Uniformity of coating and consequent long life is secured by virtue of the close control to repeat the heat cycle again and again under the same conditions.

Fig. 5 illustrates a large japanning oven such as is used by automobile manufacturers to bake the finish on the cars. This oven has 252 kw. connected capacity, and work is carried through it continuously by conveyor. Ovens turning out a car per minute and requiring over 3000 kw. to heat have been in use for several years in one automobile shop. The electric baking of japan, paints, lacquers, varnish, etc., has come to be considered a standard process in many lines of manufacture.

Tests made on a vertical type of electrically heated glass annealing lehr show a reduction in over-all cost of product of 20 per cent over that in the gas-heated lehr. This saving was equivalent to seventy-five times the cost of the electric power for heating the lehr. This type of lehr for annealing glass presents many positive advantages for rapid, uniform, and economic annealing of most commercial glass. The box type oven or lehr, electrically heated, serves with equal advantage for other types of glass, including optical and telescopic lenses. Some of these advantages are as follows: (1) High thermal economy, (2) satisfactory heat distribution, (3) small floor space, (4) possibility of location near fabricator, receiving the ware at higher temperature, (5) reduction in labor, (6) lack of opportunity for ware to absorb products of combustion, (7) low temperature gradients, (8) automatic heat control (±2.5° C. may be secured), (9) annealing time less than one-half of the present-day fuel fired lehr, (10) practical elimination of rejects, distortion, and breakage due to heat treatment, (11) freedom from sulfuring of the ware and the production of a bright polished surface requiring no subsequent cleaning and washing, and (12) a sterile and absolutely clean product, such that prescriptions where this is important, as in medicinals, may be filled in and sealed immediately after leaving lehr.

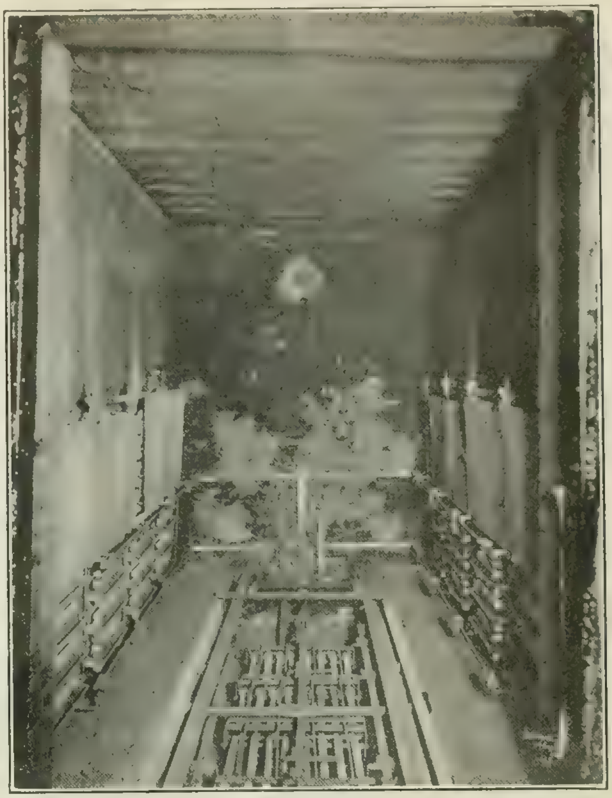

FIG. 4

A portable metallic resistor furnace, with a hearth dimension of 10.5 in. wide by 21 in. long, is ideally suited for annealing, hardening, and tempering or drawing files or small tools in the ordinary tool room. It is likewise suited to any heating requirements where the charges do not require more than 1800° F. Some of its advantages over fuel fired unmuffled furnaces are as follows: (1) Radiant heat, (2) satisfactory heat distribution, (3) automatic control of temperatures if desired, (4) practically nonoxidizing atmosphere if desired, (5) small amount of heat given off to the room, (6) no products of combustion or obnoxious gases given off to heating chamber or room, (7) ratio of heat generation to heat absorption by charge correctly maintained, (8) uniform and complete penetration of heat through charge without overheating of corners, fins, or surfaces, (9) ability to repeat desired heat cycle giving uniformity of product, (10) a reduction, generally, in labor, and (11) a better over-all economy and the production of higher quality product at the same or slightly higher cost or the same quality at a lesser over-all cost.

Fig. 6 is a view of the interior heating units, hearth and walls, of a furnace with a rotating hearth which is being used for heat treating parts in an automobile factory. Its resistors are metallic and its temperature limit is 180° F. It operates normally at 1550° F., 3 phase, 440 volts with 270 kw. connected capacity. The furnace has automatic temperature control and operates to heat such parts as engine, crank-shafts, etc.

Electrically heated furnaces are well adapted to baking vitreous enamels. One of the chief disadvantages of the coal, gas, or oil fired furnace is that the muffle periodically sags and breaks, with resultant loss of product and of time for repairs. This is avoided in the electric furnace. Another disadvantage which is not met in the electric furnace is the presence of sulfur fumes. Furthermore, even distribution of heat can be obtained only with electric installation. The furnace can be loaded from the rear wall almost to the door and burned down to a finish, leaving a clean white enamel.

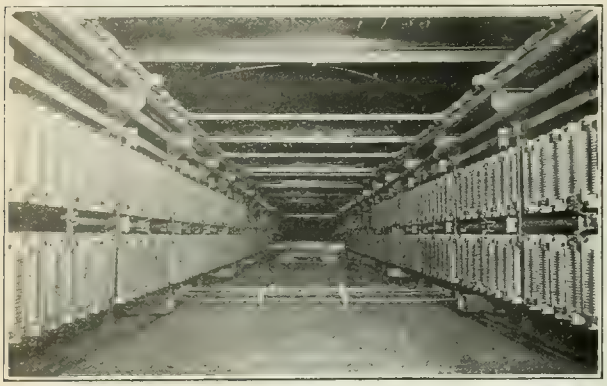

Fig. 5

The cost of the electric furnace is considerably higher in original investment, but the saving in space and cleanliness soon make the difference in price a matter of secondary importance. The power cost is also higher. However, with the additional output, tests show that the actual cost per pound of metal handled will compare very favorably with any other form of fuel. When the electric furnace is able to handle at least 170 heats in 10 hrs. against 130 heats by the coal furnace, with a 25 per cent greater weight of charge, and without a single reject, the comparison in cost of fuel assumes a different proposition, and a value actually in favor of electric heat. The electric furnace can be brought from cold to 1700° F. in 12 hrs. A coal furnace would require about 3 days, an oil furnace 24 hrs., and a gas furnace 16 to 20 hrs. The outstanding features of the furnace have been the extreme speed at which it can be heated up, and at which it can be operated. Heats have been completed in 1 min. 50 sec. that would have taken 3 min. 40 sec. in an oil furnace.

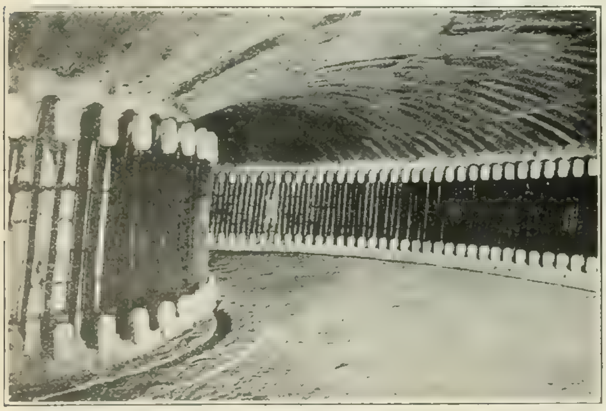

Fig. 6

The muffled arc type of electric furnace is used as a melting furnace, both of the laboratory type and in larger units. A furnace with a hearth capacity of 2000 lbs. of brass and with 250 kw. connected will melt yellow brass in pig or heavy scrap form at the rate of 1500 lbs. per hr., with a metal loss of less than 1.5 per cent and a power consumption not in excess of 270 kw. hrs. per ton. Copper is melted at the rate of 1300 lbs. per hr. with a power consumption of 350 kw. hrs. per ton.

This power consumption is based on melting not less than 1500-lb. charges and allowing 20 min. per heat for charging, pouring, and foundry delays. Such a furnace is normally provided with a tilting motor and three electrode motors, all of which are of AC type, so that the necessity for a DC motor generator set, usually required for furnishing direct current to the control motors, is eliminated. This type of furnace operates at a temperature up to and including that required for melting nickel and monel metal. A power factor of 95 per cent and better is realized, together with freedom from lead fluctuations.

Other applications of electric heating include cartridge unit heaters (similar in shape to the ordinary gun cartridge), which are used in shoe making machines, cigaret making machines, stills, sterilizers, paper cup machines, etc. Electrically heated compound melting pots find extensive use for glue in wood working shops, in battery works, book binding and printing houses, and piano, paper box, and automobile factories.

Conclusion

These few illustrations out of the many working installations in various processes have been used to indicate the applicability of electric heat to advantage throughout the whole industrial heating field. It is not to be inferred that electric heat is without a competitor in all places and under all conditions. There are, however, a very great number of applications where electric heat may be used to advantage. These applications in various processes occur with so great frequency that it behooves the user of heat processes to question his furnace engineer thoroughly concerning the possibilities of electric heating before revamping existing installations or adding new thermal process equipment.

Biscuit and Cracker Manufacturers' Association

As a next step in the development of The Technical Bureau of the Biscuit & Cracker Manufacturers' Association, the Technical Committee has been authorized to secure the services of A. V. H. Mory, well known for his success in the organization and direction of industrial laboratories. A good start has already been made in the work of the Bureau, which was launched in 1919, as another step in the direction of insuring the highest quality and uniformity for the Association's products.

Mr. Mory has had broad experience as head of the chemical department of Armour & Company's Kansas City plant, chief of the Government Food and Drug Inspection Laboratory at Kansas City, Mo., director of the Technical Laboratories of Sears, Roebuck & Co., and more recently with the Procter & Gamble Company.

The new Technical Bureau Director, who is well known for his belief in directness, simplicity, and common sense in all the relations of science to industry, will find in his new field plenty of opportunity for accomplishment.

St. Louis Meeting, American Ceramic Society

The advance announcement of the 24th Annual Meeting of the American Ceramic Society, February 27 to March 3, 1922, includes three days devoted to the presentation and discussion of papers on manufacturing problems, and two days of visiting industrial plants. Round-table discussions are planned on a large number of subjects, such as heat conductivity and insulation, abrasives, feldspar resources and deposits, raw materials for the glass industry, wet process enamels for cast iron, and glass house refractories. Forty papers are at present included on the program, and more are being added.

The Flow of Fluids through Commercial Pipe Lines[1,2]

By Robert E. Wilson,[3] W. H. McAdams and M. Seltzer

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

The information at hand concerning the flow of fluids in pipe lines is discordant, scattered, and incomplete except in a few special fields. The great bulk of the work to date has been devoted to the flow of water, from which empirical relationships and constants have been derived, but even in this case a study of the results reveals considerable disagreement among the investigators. Another range which has been carefully studied is the flow of viscous liquids, such as heavy oils and glycerol, through comparatively small tubes. Comparatively little reliable experimental work has been published on the flow of very viscous liquids through commercial pipes, and practically none has touched on the frictional resistance of elbows in viscous flow.

Certain general principles with regard to the flow of fluids are, of course, generally recognized. Thus it is well known that there are two general types of motion for liquids—usually called viscous and turbulent flow. Viscous flow is characteristic of low velocities, small pipes, or very viscous liquids. In this form of motion, all the particles move in lines parallel to the movement of the mass as a whole, though the velocity of motion drops off rapidly from a maximum at the center to zero at the outside of the pipe. The average velocity over the entire cross-section of the pipe is one-half the maximum value at the center of the pipe.[5] This form of motion is shown graphically in Fig. 1. It is to be noted that there are no "cross" or mixing currents. It is well established that Poiseuille's formula holds for this type of motion. Expressed in convenient engineering units, this takes the modified form:[6]

$$p = \frac{0.000668\, z\, l\, v}{D^2}$$

In the case of every fluid, as the velocity is increased a point is eventually reached where a rapid transition takes place from viscous flow to an eddying, mixing type of motion known as turbulent flow, and here the net velocity distribution curve is much flatter, the average velocity being about 80 per cent of that at the center. (See Fig. 1.) The transition velocity is called the critical velocity and its magnitude depends upon the viscosity and density of the liquid and the size (and roughness) of the pipe (increasing in direct proportion to the first factor, and in inverse proportion to the other two).

The formula most frequently used for turbulent flow is that of Fanning, which in engineering units can be expressed:

$$p = \frac{0.323 f\, l\, s\, v^2}{D}$$

It will be noted that the principal differences between the formulas for viscous and turbulent flow are that in the latter case the velocity occurs as the square rather than the first power, while the diameter of the pipe occurs as the first power rather than the square. Furthermore, the viscous flow formula includes the viscosity of the fluid as one factor and does not require any variable coefficient, while the turbulent flow formula apparently disregards the viscosity of the liquid, and adds a variable friction factor, f, which is a rather complicated function of velocity, pipe diameter, viscosity, density, and the condition of the pipe surface.

It is thus apparent that the above formula for turbulent flow is only a rough approximation of its true law of motion, and the results can be made accurate only by varying the values used for the friction factor f. Attempts to formulate a general equation have resulted in the use of fractional exponents for v and D, but no two writers agree as to the exact magnitude of the exponents, except to place that of v generally between 1.6 and 1.9, and that of D between 1.4 and 1.1. These attempts have failed, since these exponents hold approximately constant only over a limited range of velocity and diameter. Corrections for roughness are also a disturbing factor. One or two writers suggest putting z into the numerator of Fanning's equation with a small fractional exponent in the neighborhood of 0.4. The difficulty of using such equations in practical work is obvious.

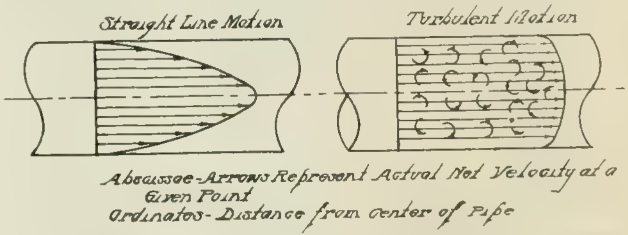
Straight Line Motion
Turbulent Motion
Abscissae-Arrows Represent Actual Net Velocity at a Given Point
Ordinates- Distance from center of Pipe

Fig. 1—Comparison of Viscous and Turbulent Flow in Pipe Lines

The object of the experimental work described herein was to fill in the gaps in the existing data on the flow of fluids in pipes of commercial size and roughness, especially for very viscous liquids and in the critical region between viscous and turbulent flow; and to determine with reasonable accuracy correction factors for the pressure drop around bends. By combining these data with a critical survey of existing information, it has been found possible to develop a simple but comprehensive method of treatment of the whole subject of the flow of all types of fluids through commercial pipe lines, using a *single* method of calculation for all types of flow.

This work was undertaken at the instigation of Dr. W. K. Lewis and has profited greatly by his suggestions and advice. Acknowledgments are also due to the National Tube Company, who supplied most of the pipe and financed the bulk of the experimental work; to the Hammel Oil Burning Equipment Company, who paid for the installation of the 4-in. pipe line and for some additional experimental work; and to the Parks-Cramer Company and The Texas Company, who supplied the oils used.

Apparatus

The installation for the experimental work is shown diagrammatically with essential dimensions in Fig. 2, and by photographs, Figs. 3 and 4. It included a 35-h.p. motor driving a rotary gear pump connected on the suction side by 4-in. pipe to a 10-ft. by 5-ft. diameter storage tank. The discharge of the pump was connected by convenient valves

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[1] Received December 10, 1921.

[2] Published as Contribution No. 40 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] Director, Research Laboratory of Applied Chemistry, M. I. T.

[4] Assistant Professor of Chemical Engineering, M. I. T.

[5] This may be proved mathematically, from the definition of absolute viscosity (see Lamb, "Hydromechanics of Fluids," 1916) and has been verified experimentally by Stanton and Pannell [Collected Researches, National Physical Laboratory, Teddington, England, **11** (1914)].

[6] The following nomenclature is used throughout this paper:

f = friction factor (Fanning)
l = length of pipe (ft.)
v = average linear velocity in pipe line (ft./sec.)
z = viscosity in centipoises (= relative to water at 68° F.)
p = pressure drop (lbs./sq. in.)
s = specific gravity of liquid
D = inside pipe diameter (in.)
Q = flow (gal./min.)

The precise definition and measurement of these quantities is discussed later.

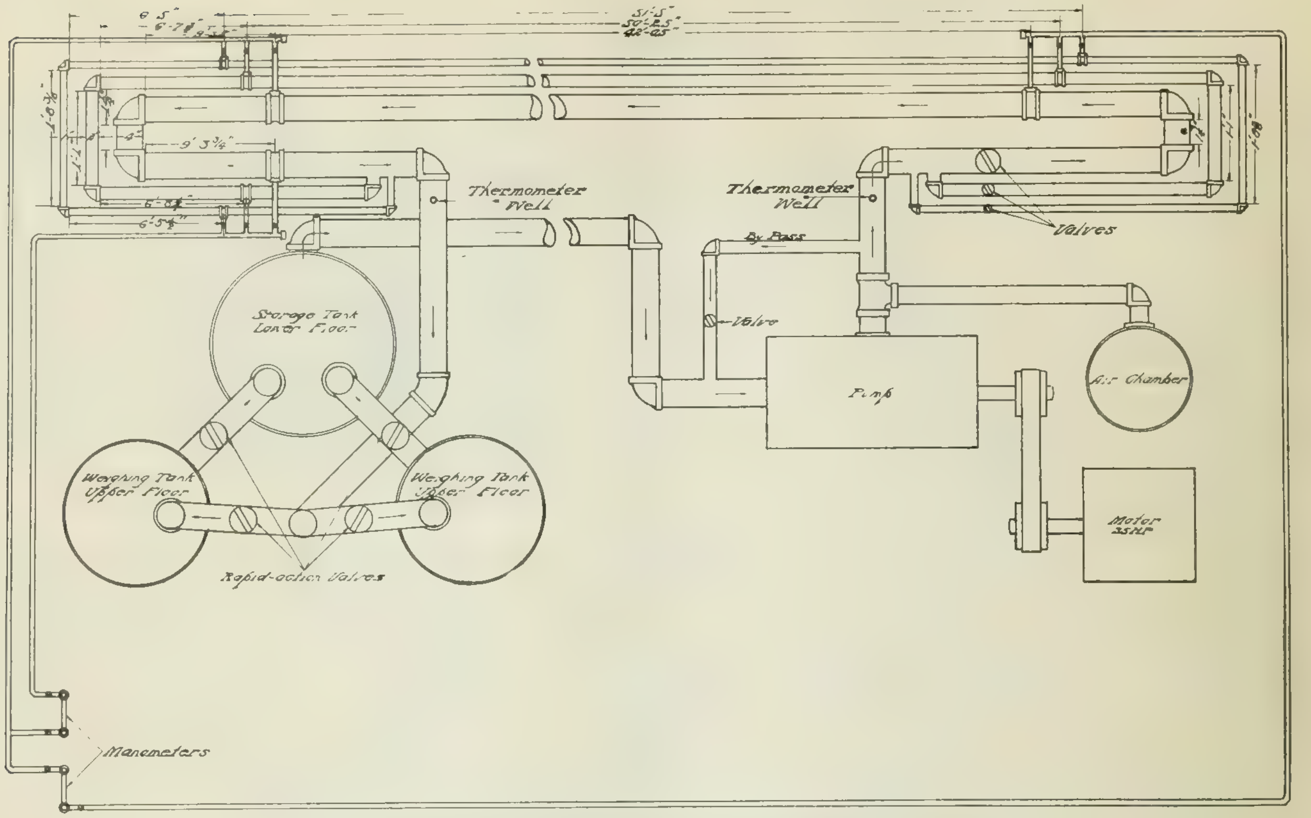

Fig. 2—Diagrammatic Layout of Apparatus for Pumping Viscous Liquids
(Not drawn to scale)

to about 150 ft. each of 4-in., 2-in, and 1-in. "Welding Scale Free" standard steel pipe, made by the National Tube Company. The actual diameters were measured and found to correspond within the limits of error to the standard dimensions (Table II). These lines led to a common 4-in. riser equipped with quick-acting valves leading to two weighing tanks 5 ft. by 4 ft. in diameter. The weighing tanks were on the floor above storage tank, which conveniently allowed the liquid to flow back to the storage tank by gravity. The pressure drop was measured by means of a vertical glass U-tube about 10 ft. high containing water on mercury, which measured pressure differences up to 100 lbs. per sq. in. This manometer was connected by $^3/_8$-in. pipe lines to include either 42.04 ft. of 4-in. straight pipe, 50.21 ft. of 2-in. straight pipe, or 51.42 ft. of 1-in. straight pipe by valve manipulation. The straight pipe was continued about 10 ft. on each side of manometer connections to eliminate all effect of the bends. The manometer pipe lines containing oil led to a 3-in. diameter chamber above the manometer half full of water, while the lines from this chamber to the mercury manometer were full of water. This scheme allowed instantaneous pressure readings, despite the high viscosity of the oils. The pressure drop in lbs. per sq. in. for this system can readily be shown to be $\frac{(13.6-1) \times 14.7}{13.6 \times 2.54 \times 30}$ or 0.179 times the manometer reading (R) in cm. A similar but smaller manometer measured the pressure drop around the bends, which in each case consisted of two standard 90° elbows (in the three pipe sizes listed above) connected by a close nipple, with straight pipe leading to the manometer connections which were from 6 ft. to 10 ft. on each side of the bends. The storage tank was equipped with a steam coil for heating the liquids. Mercury thermometers were provided to indicate the temperatures of the oil at entrance and exit, while a by-pass around the pump afforded adequate control of the flow. A large air chamber beyond the pump served to damp out pressure fluctuations.

PROCEDURE

A series of runs was made at a definite oil temperature varying from low to high rates of flow and vice versa. The whole system was first brought to a condition of steady flow, and then suddenly switched into the empty weighing tank, recording the time with a stop watch. The average duration of an individual run was from 1 to 4 min., during which time the discharge was accurately weighed, the pressure drops in the straight pipe and around the bend were noted, and the entrance and exit temperatures were read. A series of seven to ten runs at different velocities was made with each oil at each temperature. The total number runs made in the course of the experiments was about 400.

As noted previously, the "pressure drop around the bend" included the drop due to two elbows and three connecting sections of straight pipe. In order to calculate the effect due to the elbows alone, a correction obviously had to be made.

The pressure drop through the straight pipe between manometer connections (excluding the two elbows) was calculated from the data secured at the same time on straight pipe alone, and this amount was subtracted from the total pressure drop around the bend as measured by the manometer. This value divided by two gave the pressure drop for one standard 90° elbow.

Four different oils were used in the course of this investigation. They may be briefly described as follows:

1—Mexican petroleum, a crude asphalt base oil, one of the most viscous oils handled commercially, was used to obtain data in the upper[7] viscous flow region.

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[7] The words "upper" and "lower" in this paper refer to regions with comparatively high or comparatively low values of *f* as indicated on Fig. 12, etc.

2—For the lower[7] part of the viscous flow region, recourse was had to Meprolene, a refined paraffin base oil used in oil heating systems. This oil had a somewhat lower viscosity than the Mexican petroleum and could be heated much hotter without changing in composition, so it was used over a wide range of viscosities.

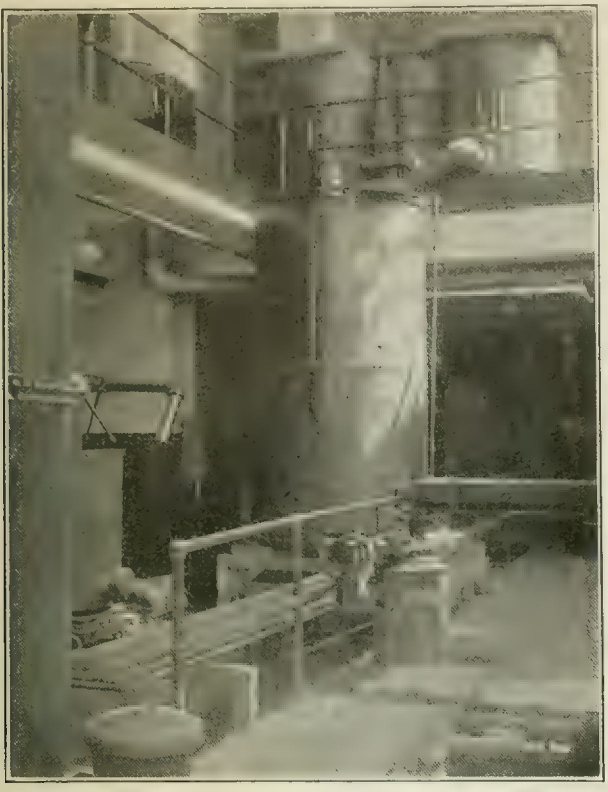

FIG 3—SHOWING TWO WEIGHING TANKS (ABOVE), STORAGE TANK, AND ONE END OF PIPE LINES

3—Port Arthur light crude, a rather fluid fuel oil, was used to cover the upper portion of the turbulent flow region, in which few data were available.

4—Modified Port Arthur, made by adding one barrel of Mexican petroleum to fourteen barrels of the above oil, was employed in order to get a series of points in, and on both sides of, the critical range.

Table I summarizes all essential information with regard to the four oils.

TABLE I

		GRAVITY AT 70° F.		VISCOSITY CENTIPOISES		VISCOSITY SAYBOLT SECONDS	
OIL	SOURCE	SP. GR.	° BÉ.	70° F.	100° F.	70° F.	100° F.
Mexican Petroleum	Hammel Oil Burning Equip. Co.	0.962	15.7	4370	970	20700	4700
Meprolene	Parks-Cramer Co.	0.900	25.4	3400	815	17100	4200
Port Arthur Light Crude	The Texas Company	0.903	25.0	65.7	30.7	330	157
Modified Port Arthur	The Texas Company	0.910	23.8	86.0	39.6	430	202

The viscosity-temperature curves for the four oils are shown on Fig. 5.

The results obtained from the 400 runs on the four oils, together with those in the literature on the flow of water, air and steam, and a little on oil, were sufficient to cover the whole range of conditions likely to be encountered in commercial practice.

DISCUSSION OF RESULTS

METHOD OF PRESENTATION—The reader who is interested solely in the practical use of the methods of calculation herein recommended may well refer at once to the later section describing only the recommended methods of calculation. However, in order to present the basis for and show the validity of these final conclusions, it is necessary to discuss in some detail the theory and existing data pertaining to the flow of fluids.

The engineer who is habitually making calculations for the flow of a given type of fluids through pipe lines is usually able to assemble from various sources some data or empirical equations applicable with fair accuracy to the particular set of conditions in which he is interested, and to develop a reasonably satisfactory procedure for making the necessary calculations. Even for the comparatively simple case of water, however, interpolations must be made from values given in tables for arbitrary friction factors, and the values given by two different references are likely to vary by as much as 30 or 40 per cent. Furthermore, no mention is made in most texts on hydraulics of the possibility of straight line flow for water, which does take place in small tubes at moderate velocities. The use of the customary formula in this range will cause enormous errors.

Much less fortunate, however, are the majority of chemists and engineers who have but infrequent occasion to make such calculations, especially if they venture out of the beaten path of the flow of water, air, or steam. Fundamental exposition of the general laws of flow are rare, usually highly mathematical, and expressed in absolute units. Practical data, on the other hand, are scattered in many different periodicals, expressed in a wide variety of units, and generally cover only a narrow range of data on a given article. In the typical reference handbooks different empirical formulas are given for the flow of air, steam, and water, but even with the aid of all the foregoing information it is impossible for one unfamiliar with the subject to calculate the rate of flow of an oil, knowing merely the Saybolt seconds, or of a gas, knowing its viscosity. As a result of this situation, the average engineer has almost completely lost sight of the fact that *all* fluids obey identically the same fundamental laws of flow.

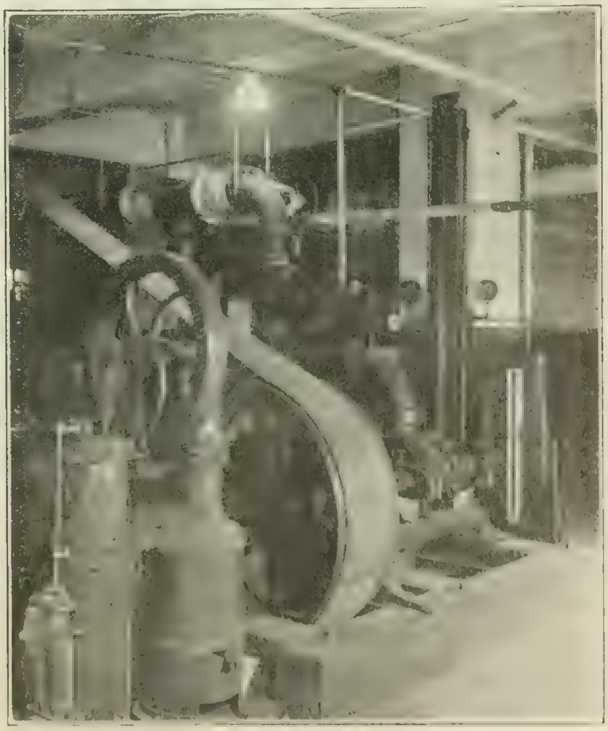

FIG. 4—SHOWING PUMP AND MANOMETERS

Most of the foregoing difficulties are due simply to the failure to treat the whole subject of the flow of fluids in a comprehensive manner and in a place readily accessible to the average individual. There are, however, two more serious difficulties which are somewhat harder to solve satisfactorily: first, the fact that the two kinds of motion follow two different formulas, which greatly complicates the calculations required to be certain of the correct result; and second, the fact that in the formula for turbulent flow there is a variable coefficient f, which is a somewhat indefinite function of velocity, pipe diameter, viscosity, density, and condition of the pipe surface.

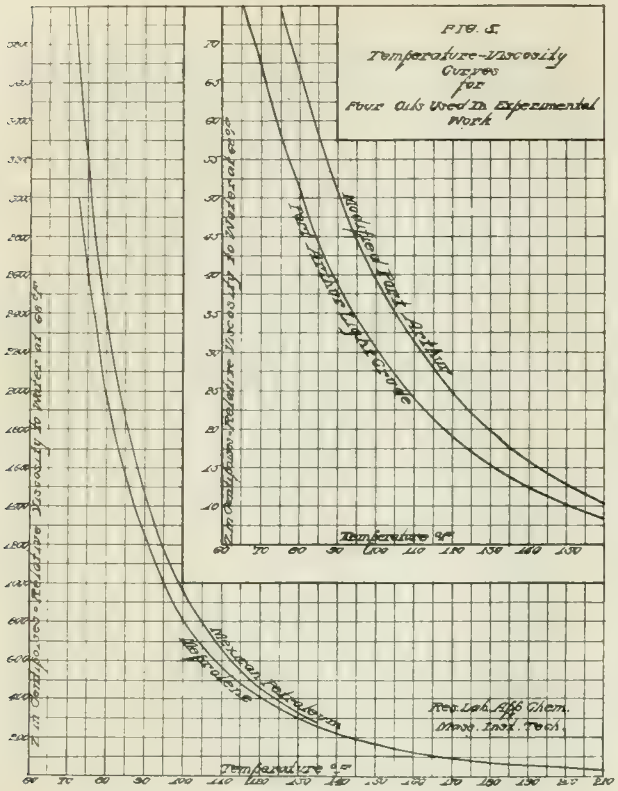
FIG. 5
Temperature-Viscosity Curves for Four Oils Used in Experimental Work

When dealing with water alone, where the density is substantially constant, and variations in viscosity are usually disregarded (though they should not be), it is of course possible to meet the situation fairly well by the use of tables showing the value of f for different velocities and pipe sizes. When, however, an attempt is made to extend the formula to cover other liquids and gases, thus bringing in two additional variables, viscosity and density, which affect f, the situation apparently becomes well-nigh hopeless. As a result the common practice has been to work out separate formulas or flow tables holding over certain ranges for each of the common fluids, and to leave the rest of the subject to be covered by some very rough general formulas, frequently with fractional exponents *applicable only over a limited range.*

Fortunately, however, it has been predicted, apparently first by Stokes[8] in England about seventy years ago, and since then rediscovered by several others[9] interested in the theoretical side of the flow of fluids, that although the variable friction factor f is a function of the four variables above mentioned, it is not an *independent* function of these quantities, but a function only of the expression $\frac{Dvs}{z}$.[10] This obviously makes possible a great simplification in the treatment of the subject, but it has unfortunately been mentioned almost exclusively in highly mathematical papers dealing primarily with the *theoretical* side of the flow of fluids.

In 1912 Blausius[11] gave a good review of the theory, recalculated the data of Saph and Schoder[12] for water in smooth brass and galvanized iron pipes and the data of Nussett[13] for compressed air, and showed that f was a function of $\frac{Dvs}{z}$, as required by the theory. This paper has apparently been almost completely overlooked outside of Germany.

By far the most thorough existing treatment of the subject from this point of view is in connection with the recent work (during the war) of the British National Physical Laboratory,[14] who used the method in the presentation of accurate data over a wide range. This work of the N. P. L., primarily on air and water, in very smooth tubes up to 3 in. in diameter, definitely substantiated for these conditions the prediction of Stokes and others that the friction factor f is, within the limits of error, a function of the simple ratio $\frac{Dvs}{z}$ rather than an independent function of the separate variables. These important results have received surprisingly little attention in this country.[15]

While the method of treatment hereinafter followed is based primarily on this valuable work of the National Physical Laboratory, the following modifications or amplifications of that work have been made in this article:

1—For the sake of convenience in practical use, all results are expressed in English engineering units, rather than absolute or metric units.

2—Less emphasis is placed on the unstable region of flow between viscous and turbulent motion.

3—Extensive data have been obtained on commercially smooth pipes with standard couplings, which are shown to give different results from the extremely smooth drawn brass tubes used by the N. P. L.

4—Data have been secured, mainly from the literature, on much larger sizes of pipe than the comparatively small tubes used by the N. P. L.

5—Many more data have been secured on the flow of highly viscous liquids through commercial pipes.

6—Complete details are given to make possible the use of a *single* method of calculation for *all* types of flow, which is highly desirable from a practical standpoint.

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[8] Math. and Phys. Papers, Vol. III (1850), 17.

[9] Reynolds, *Trans. Roy. Soc. London*, **1883**, 935; Helmholtz, "Wissenschaftliche Abhandlungen," I (1873), 158; Rayleigh, *Phil. Mag.*, **48** (1889), 321; Lamb, "Hydrodynamics of Fluids," Cambridge Univ. Press, 4th Ed., 656.

[10] This is due to the fact that f is a factor "without dimensions," and hence can only be a function of another expression without dimensions. The only combination of the four factors D, v, s, and z which cancels out all dimensions, is the expression $\frac{D\ v\ s}{z}$. It is not necessarily independent of the *units* used, unless consistent *absolute* (either English or French) units are used for all quantities, which is not the case in this article.

[11] *Z. Ver. deut. Ing.*, **56** (1912), 639.

[12] *Trans. Am. Soc. Civil Eng.*, **51** (1903), 253.

[13] "Mitteilungen über Forschungsarbeiten," 44.

[14] Collected Researches, National Physical Laboratory, Teddington, England, Stanton and Pannell, Vol. 11 (1914), and Pannell and Higgins Vol. 13 (1916). This is hereafter called the "N. P. L." data and curves.

[15] Since this paper in preliminary form was presented at the Chicago meeting of the American Chemical Society (September 1920) an article by A. C. Preston has appeared in *Chemical and Metallurgical Engineering*, for September 29 and October 6, 1920, which presents some of these results in graphic form. The Kinney Manufacturing Company and the King-Knight Company have also published two editions of an excellent booklet of the flow of oils which makes use of these N. P. L. data and method of presentation. Buckingham also discusses these data mathematically in the *Trans. Am. Soc. Mech. Eng.*, **37** (1915), 263.

In making use of the fortunate fact that f in Fanning's equation is a function of $\frac{Dvs}{z}$ rather than of all the variables independently, the obvious way to present experimental data is to plot the values of f, calculated from Fanning's equation for a given set of observations, against the corresponding value of $\frac{Dvs}{z}$.

At first sight this method of presentation would seem applicable only in the region of turbulent flow, since a different law, Poiseuille's (where $p = 0.000668 \frac{lvz}{D^2}$), is known to hold for the region of viscous flow. However, by comparing this equation with Fanning's ($p = 0.323 \frac{f\,l\,s\,v^2}{D}$), it will be noted (as pointed out by Blausius) that if $f = 0.00207 \frac{z}{Dvs}$, the two equations become identical. Furthermore, values of f which fulfil the latter equation must all lie on a line (straight on a logarithmic plot) on the above-mentioned plot of f against $\frac{Dvs}{z}$. It is therefore possible to calculate all experimental results, regardless of the type of flow, on the basis of Fanning's equation, and plot the resulting values of f, which should approximate the above-mentioned line if Poiseuille's law holds for a given case. Conversely, by referring to such a diagram for the values of f corresponding to a given value of $\frac{Dvs}{z}$, it becomes possible to calculate the pressure drop for *any* condition of flow using only a single formula (Fanning's).

This method of presenting data is therefore used throughout the following discussion. It may be well at this point for the reader to refer to Fig. 12, which shows the value of f (plotted logarithmically) over substantially the entire range of conditions met with commercially. For convenience in the presentation of experimental results, this curve has been enlarged, divided into three sections, and the data pertaining to each one discussed separately.

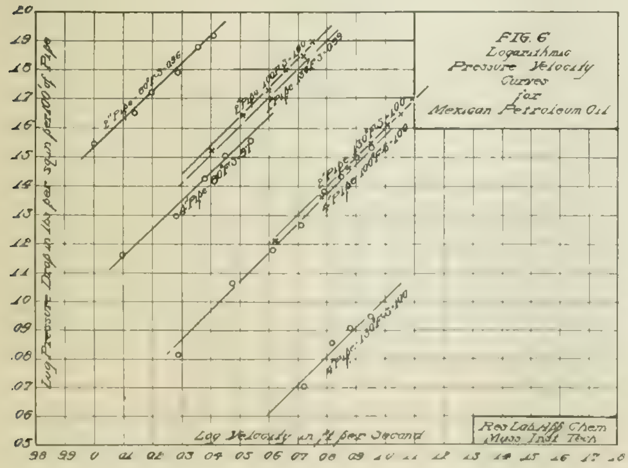


FIG. 6
Logarithmic Pressure Velocity Curves for Mexican Petroleum Oil

DATA IN VISCOUS FLOW REGION—Three sets of runs have been made by this Laboratory in the viscous flow region—one with Mexican crude in the highest viscosity region; one with Meprolene over a wide intermediate range of viscosities obtained by varying the temperature; and a few results with modified Port Arthur in the smaller sizes of pipe.

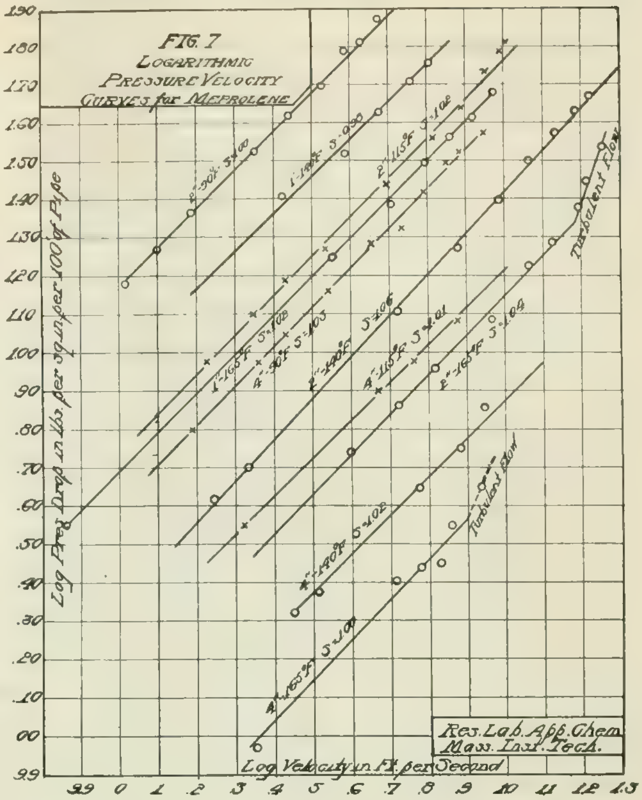


FIG. 7
Logarithmic Pressure Velocity Curves for Meprolene

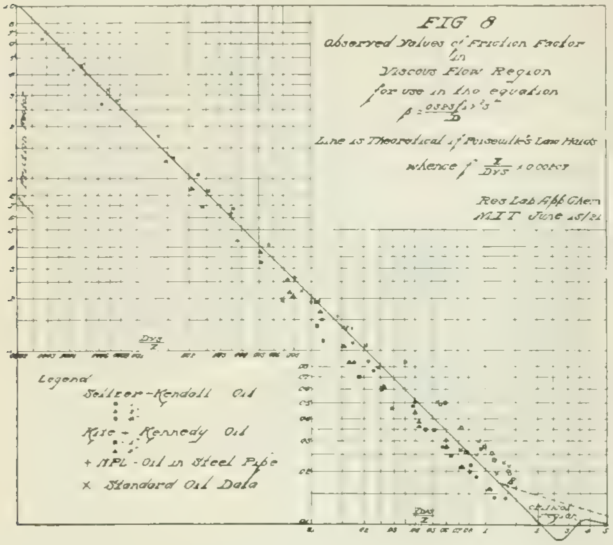
The individual observations on the first two oils are most definitely shown in Figs. 6 and 7, where the logarithm of the velocity is plotted against the logarithm of the pressure drop in each series of runs in which the viscosity and pipe size were kept constant. This is a convenient method of checking up on the variability of individual results and showing a large number of points in which all the data with regard to a given run are evident from an inspection of the plot (which is not true when the observed value of f is merely plotted against $\frac{Dvs}{z}$, as in Fig. 8).

Through each of these series of points the best representative line has been drawn and the slope is indicated in the figures. According to Poiseuille's law the pressure drop should be proportional to the velocity and these slopes should equal 1.00. Actually they are found to vary from 0.95 to 1.06, with an average of 1.01. As far as the velocity-pressure drop relationships are concerned, therefore, Poiseuille's formula appears to hold within the limit of error of the experiments, which is rather high in case of the heated oils in viscous flow because of the nonuniform distribution of temperature throughout the pipe. It will be noted that the concordance of the individual points with the line is satisfactory in substantially all cases. Data on the Mexican petroleum in 1-in. lines are omitted because (on account of the high frictional resistance) the temperature of the oil rose as much as 10° or 12° in passing through the pipe and it was impossible to get reproducible or concordant results.

It will also be noted that two of the lines show breaks in the slope, indicating a change from viscous to turbulent flow in the cases of the 2-in. and 4-in. pipes with the hottest oil (165° F.).

Since the number of individual observations in this range was so large, the method of checking up the results as a whole (as to the effect of viscosity and pipe size as well as velocity) by plotting the calculated values of f was not applied to each individual observation, but to three points—

one from the middle and one from either end of each of the lines shown in Figs. 6 and 7. The points thus obtained are shown graphically in Fig. 8. It will be noted that in the upper portion of the plot they agree very well, but in the lower portion the majority of the points determined by Seltzer and Kendall fall below the theoretical line. This deviation is unquestionably due to the fact that all results lying in this region were obtained by the use of the Meprolene heated to a fairly high temperature. In such cases there is a very wide temperature gradient between the warm center and the cold outside of the pipe, due to the absence of any convection or mixing currents in viscous flow, and it is practically impossible to make an accurate measurement or calculation of the *effective* average temperature. The temperatures used in the calculations were measured by thermometers in wells in the 4-in. pipe line just beyond the entrance and exit of the 2-in. and 1-in. lines, as indicated in Fig. 2. The thermometer therefore recorded a temperature nearer to that of the pipe and the outside cool layers of the oil than to the true average effective temperature, since most of the flow was undoubtedly taking place in the hot center core. The theoretical values of the friction factor corresponding to these high values for the viscosity were, therefore, higher than the observed points in the region where measurements were made on hot oil. The deviation averaged about 17 per cent in the highest temperature runs, and was worst, as might be expected, in the 1-in. pipe, where the velocity through the 4-in. exit line was extremely low. An error of only 3° or 4° in the effective average temperature would account for the above divergence.



In order to obtain some further data another brief series of runs was made by Kite and Kennedy covering the lower portion of this region, using the modified Port Arthur oil at ordinary temperatures. For some unexplained reason (possibly an error in the viscosity determinations) the results of this series of runs (hollow squares on Fig. 8) were about as much above the theoretical line as the other series were below, the average of the two checking the theoretical line very closely.

The only other satisfactory data on viscous flow of heavy oils through commercial pipes appear to be the single set of experiments of the N. P. L., and some results of the Standard Oil Company of California on pipes up to 12-in. diameter, published in their bulletin on the California Oil Pipe Line. Representative points from both of these sources are also recorded on Fig. 8. In calculating over the latter results use was made of a table of viscosities, privately communicated by the Standard Oil Company, correcting the data given in the booklet.

Considering the results as a whole, while there is considerable variation both above and below the line, due to factors such as frictional heating in the pipe and variations in temperature between the inside and the outside, there can be no real doubt as to the essential validity of Poiseuille's formula for viscous flow in pipes of commercial size and roughness. Since the same law has been checked up very closely for all types of liquids in extremely smooth glass and metal tubes, it is evident that the roughness of the pipe is a comparatively small factor in determining the resistance to viscous flow—as might indeed be anticipated on theoretical grounds, since there is in any case a practically stationary and fairly thick film of oil on the inside surface of the pipe. It will be noted that this conclusion is quite different from that drawn from results obtained in the turbulent flow region.

DATA IN CRITICAL AND UPPER TURBULENT FLOW REGIONS—Possibly the most interesting, and at the same time the most troublesome, portion of the subject of the flow of fluids is the critical region between viscous and turbulent flow. Fig. 8*a* brings out the essential facts as they appear from a careful study of the various experiments (usually in small tubes) described in the literature.[16] The solid lines are the portions of the viscous and turbulent flow curves about which there is little doubt; the turbulent flow line extended to the left intersects the viscous flow line at Point 1 frequently referred to as the "minimum" critical point. The weight of evidence seems to indicate that these two intersecting lines represent the most stable conditions of flow, it being noteworthy that the type of motion giving the *largest* value of f (and hence the greatest dissipation of energy) for a given value of $\frac{D\,v\,s}{z}$ is the one which tends to prevail.

Actually, however, it is observed in careful laboratory experimentation that viscous flow has a marked tendency to perpetuate itself under conditions where turbulent flow would be expected, while the opposite tendency has never been noted. If, for a given liquid flowing through a given pipe, the velocity (and hence $\frac{D\,v\,s}{z}$) is gradually increased and no disturbing influences are present, the observed values of f tend to follow the dotted extension of the viscous flow line for some distance beyond the lower critical point, and observations to determine the type of flow by means of colored threads of liquid indicate that it is still viscous. Sooner or later, however, a point is reached where the flow suddenly changes to turbulent and the values of f quickly rise to the turbulent flow line, as indicated on Fig. 8*a*. There is wide disagreement as to the exact location of this "higher" critical point,[17] the evidence indicating that, as would be expected for an essentially unstable type of flow, it varies greatly with conditions; many disturbing factors, such as surface roughness in the pipe, the presence of valves and fittings, changes in cross-sectional area, vibrations, turbulence of the entering water, all tend to make the change from viscous to turbulent flow come sooner than under more ideal conditions.

Properly speaking, therefore, reference should be made to a critical *region*, rather than to a critical point or points. Furthermore, most authorities state that if this critical region is entered by gradually *lowering* the velocity from the turbulent flow side, the tendency is to follow the dotted turbulent flow line clear over to the point of intersection, without any abnormal dip in the observed values of f. Experimental results seem to indicate, however, that while turbulent flow tends to persist longer under these conditions, it may nevertheless return to viscous flow before Point 1 is reached.

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[16] Lamb, "Hydrodynamics," 4th Ed. (1916), Cambridge Univ. Press, 651; Russell, "Textbook of Hydraulics" (1908), 110; Reynolds and Osborne, *Proc. Roy. Soc. London*, **35** (1883), 94; Barnes and Coker, *Ibid.*, **74** (1904–5), 341.

[17] There is also some disagreement in the literature as to whether Point 2 or 3 should be called the higher critical point.

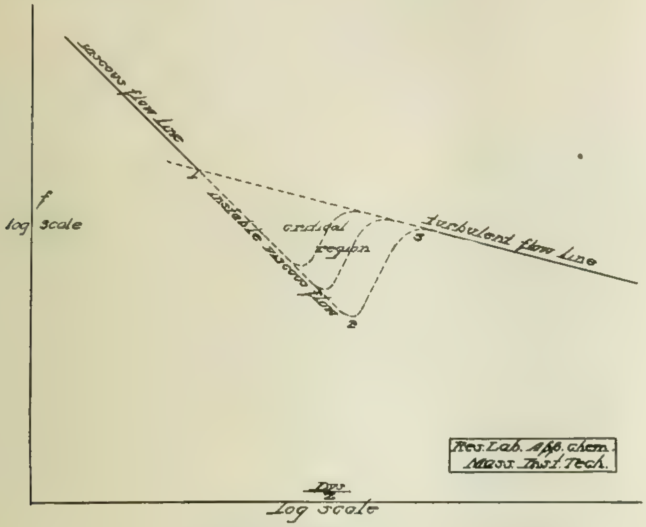


Fig. 8a—Diagrammatic Representation of Different Flow Curves Obtained in the Critical Flow Region

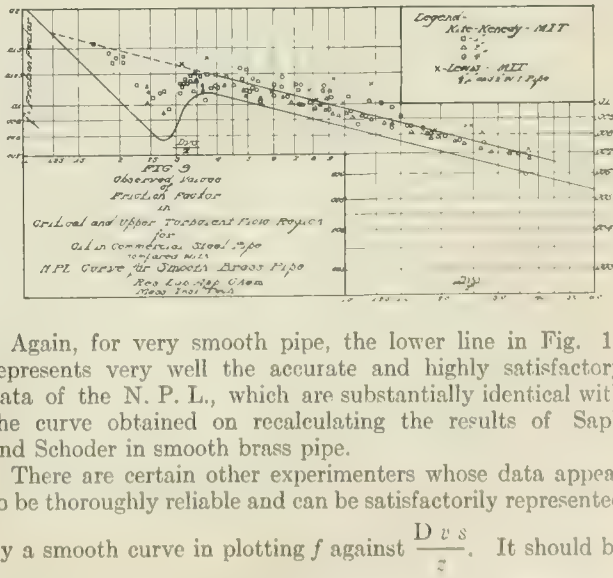
The N. P. L., working with extremely smooth tubes, have obtained the most consistent series of data in this region which has thus far been available, practically all their points falling within 3 or 4 per cent of the curve shown in Fig. 9. (The number of points determined by the N. P. L. is so large that reference must be made to the original article for such details.) The recalculated data of Saph and Schoder[12] also check this curve very well, showing that, with very smooth pipe, even the critical region gives fairly consistent values of f when plotted against $\frac{D\,v\,s}{z}$. The abnormal dip in the curve as determined by them is both wider and deeper than would be indicated by a few experiments under commercial conditions, though it is less pronounced than has been found by some experimenters under ideal conditions in glass tubes.

In view of the almost complete lack of accurate data for commercial pipes in this region, this Laboratory undertook a rather extensive investigation of the phenomenon in 1-in., 2-in., and 4-in. pipes, with the Port Arthur light crude and modified Port Arthur oils, the results of which are shown in Fig. 9. Since the observed points indicate a much smaller dip in the critical region for commercial pipe than is found by the N. P. L. (undoubtedly due to surface roughness, the presence of couplings, vibrations, etc.) and furthermore, since the presence of other disturbing factors or special operating conditions are at any time likely to bring the pressure drop up to the theoretical line for turbulent flow, it appears to the authors that the proper treatment of this region for *practical* purposes in *commercial* pipe lines is to assume the turbulent flow line as extending straight over to the viscous flow line, thus simplifying the treatment and being on the *safe side* in all calculations. This would, of course, lead to slight errors if the pressure drop through a commercial pipe line were used as a measuring system in this region of flow, but no such method of measurement, regardless of the friction factors assumed, can give reliable and reproducible results in this unstable region.

This method of treatment indicates that the critical velocity for *commercial* pipes occurs when $\frac{D\,v\,s}{z} = 0.12$ or $v = \frac{0.12\,z}{D\,s}$, which is much lower than the values based on work in glass tubes, which are the ones customarily quoted in reference books. As indicated above, however, the flow is variable and uncertain for values of $\frac{D\,v\,s}{z}$ between 0.12 and 0.4 (or possibly even higher under ideal conditions) and reference should be made to a critical region rather than to a critical point or points. Fortunately, in the method of calculation recommended hereinafter there is no need whatever of knowing the critical velocity, since the same formula is used for both types of flow.

Considering next the upper part of the turbulent flow region, also shown in Fig. 9, the data obtained in this Laboratory by Kite and Kennedy, and by Lewis,[18] appear to be the only reliable data for commercial pipes in this region, although there are a considerable number available in the lower part of the turbulent flow region. It will be noted that the concordance of the points (except a few of Lewis') is much better than it was in the viscous flow region, owing to the fact that in turbulent flow the temperature is substantially constant throughout the pipe, and that variations in viscosity have much less effect in turbulent than in viscous flow. Furthermore, there is no consistent difference between 2-in. and 4-in. pipes, though the 1-in. results appear to average very slightly higher. The results are, however, consistently higher than those obtained by the N. P. L. on smooth pipe in the same region—the divergence averaging about 15 per cent. Unfortunately, practically no other data are available to serve as a check upon these results, but as will be noted later from a consideration of Fig. 10, the results are entirely consistent with those obtained by many observers in the lower part of the region.

DATA IN LOWER TURBULENT FLOW REGION—This Laboratory has secured no original data in the lower turbulent flow region, primarily because this appeared to be well covered by the results of a number of other experimenters both in very smooth and in commercial pipe.



Again, for very smooth pipe, the lower line in Fig. 10 represents very well the accurate and highly satisfactory data of the N. P. L., which are substantially identical with the curve obtained on recalculating the results of Saph and Schoder in smooth brass pipe.

There are certain other experimenters whose data appear to be thoroughly reliable and can be satisfactorily represented by a smooth curve in plotting f against $\frac{D\,v\,s}{z}$. It should be understood that most of these data were not presented in this form by the original authors, but have been recalculated

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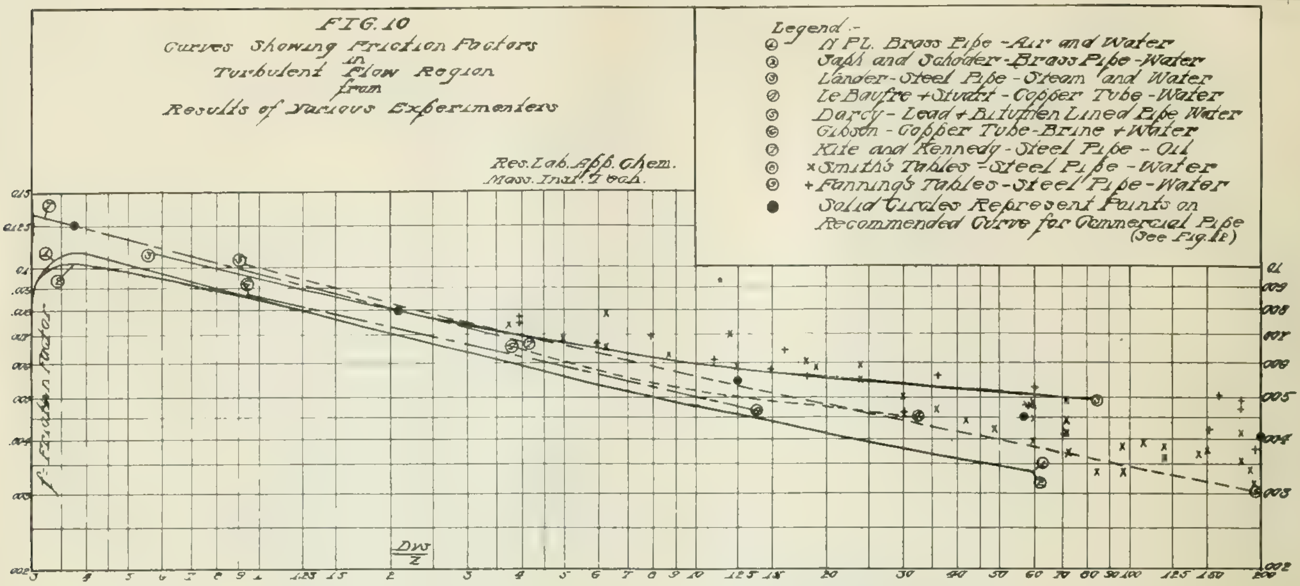
[18] This Journal, 8 (1916), 627.



1—N. P. L., *Phil. Trans.*, **1914**, A, 199.
2—Saph and Schoder, *Proc. Am. Soc. Civil Eng.*, **51** (1903), 253.
3—Lander, *Proc. Roy. Soc. London*, **1916**, A, 337.
4—Le Baufre and Stuart, *Trans. Am. Soc. Mech. Eng.*, **1919**, 655.
5—D'Arcy, *Compt. rend.*, **38**, 407.
6—Gibson, *Proc. Inst. Mech. Eng.*, **1914**, 201.
7—Hamilton Smith and Fanning, "Hydraulic Tables."
8—Hughes and Safford, "A Treatise on Hydraulics," 331.

either by the N. P. L. or by this Laboratory to put it in this more convenient form. Curves are in no cases drawn unless there is a reasonably good concordance among the points when thus calculated and plotted.

Considering briefly the other lines on Fig. 10, the results of Gibson with brine solutions in smooth copper tubing are also only slightly above the N. P. L. curve. The work of Le Baufre and Stuart on condenser tubes of Admiralty metal is still slightly higher than these results.

Undoubtedly, the best results on commercial steel pipes are the comparatively recent and extensive results of Lander, in England, who used steam and water flowing through steel pipe and obtained a very concordant series of results when plotted against $\frac{Dvs}{z}$. It will be noted that the upper part of Lander's curve checks very closely with that derived in this Laboratory for oil, while the lower part is still further above the curves for smooth pipe.

It would logically be expected that the tables given in reference books on hydraulics for the values of f as a function of pipe diameter and viscosity would be the most satisfactory for the purpose of determining the proper curve to represent the extensive results on water in commercial pipes. The tables compiled by Fanning and those by Hamilton Smith are those most generally recognized and copied for this purpose.[19]

It was soon found, however, that plotting the values given by these authors against $\frac{Dvs}{z}$ gave widely scattering points, as is shown in Fig. 9. Furthermore, deviations between the values given by the two authors were sometimes as great as 30 per cent (mostly in large pipes). A careful consideration of the results indicated further that, if these tables are correct, f is not a function of $\frac{Dvs}{z}$ for very large pipes such as are used in water mains.

Being somewhat reluctant, however, to accept this conclusion, the authors made an effort to resurvey the original data on which Fanning and Hamilton Smith based their tables. This inspection readily showed the difficulties encountered in attempting to work out these tables for very large pipes. In practically every case the data obtained by a given experimenter covered only one size of pipe, and, furthermore, no attempt was made to measure the temperature of the water. Since the viscosity of water varies about 25 per cent for a variation of 20° F. it is undoubtedly an important cause of the discordant results reported. Other variations were undoubtedly caused, even in comparatively new pipes, by wide variations in roughness due to tuberculations, etc., on the surface of the pipes. Being compelled to derive formulas from this kind of scattered and unreliable data, especially for the larger pipes, it is obvious that considerable errors might be made in interpolating and extrapolating results to cover the whole field.

The authors therefore reached the conclusion that the tables derived by Fanning and by Hamilton Smith were as good as could be worked out, considering the type of data which was available to them, but that the wide scattering of the values of f when plotted against $\frac{Dvs}{z}$ does not in any sense prove that f is not a function of $\frac{Dvs}{z}$. Typical individual points from the tables of these two authors are shown in Fig. 10. While the deviations are obviously large, their average deviation from the recommended curve for f is no greater than that between the two tables themselves in the cases of the larger pipes. The results also indicate clearly that for commercial pipes, especially for high values of $\frac{Dvs}{z}$, the values of f are very much higher than those obtained by the N. P. L. in smooth pipe.

It should be pointed out that for a given value of $\frac{Dvs}{z}$ both tables tend to give higher f's for pipes of smaller diameter working at correspondingly higher velocities. This might appear to indicate that for very large pipes the effect of a given degree of surface roughness became relatively less, and that all large pipes gave results similar to the N. P. L. for very smooth pipe; on the other hand, it might merely be due to the fact that the large pipes were usually bitumencovered wood and hence somewhat smoother than ordinary cast iron or steel. These results cannot, however, be given as much weight as those of Lander, which were obtained under much more carefully controlled conditions, although not in such very large sizes of pipe.

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[19] For both sets of tables see Hughes and Safford, "A Treatise on Hydraulics," p. 331.

From a careful consideration of these results, this Laboratory has determined (see Fig. 12) what it believes to be the best values of f for clean commercial pipes, at least those from 1 in. to 8 in. in diameter, in the light of all experimental data at present available. For larger pipes the best value of f probably deviates toward the lower curve for very smooth pipes. For very rough or tuberculated pipes the friction factors may, of course, be much higher than the values given for commercially smooth steel or cast-iron pipes. The recommended line is not drawn in Fig. 10 because it would tend to obscure the other lines, but the solid circle indicates its location as drawn in Fig. 12.

This completes the consideration of the data on the flow of all fluids in both smooth and commercial pipe lines. The recommended friction factors for use under all conditions are shown in Fig. 12, as above noted. The mathematical significance of these lines, and the recommended methods of calculation, are discussed in later sections.

RESISTANCE TO FLOW THROUGH ELBOWS—The subject of the flow through elbows is another on which the data are very incomplete. The most convenient method of expressing the frictional resistance due to an elbow of given size is in terms of the equivalent length of straight pipe which will give the same resistance to the flow of a given liquid. The published results on this subject have indicated that the equivalent length of pipe in feet was nearly independent of velocity, but was almost directly proportional to the size of the elbow, and it has therefore become customary to express this equivalent length in terms of pipe diameters, rather than feet, so that the figure will be substantially the same for all sizes of pipe.

Expressed on this basis, the customary recommendation of handbooks is to allow from 30 to 50 pipe diameters for each elbow in a line. An inspection of the data indicates that this rule is fairly well justified for the case of water (though the figure of 50 pipe diameters is well on the safe side of most of the results). There are, however, comparatively few data in the upper part of the turbulent flow region, and apparently none whatever in the critical or viscous flow regions.

Fig. 11 presents in graphic form the results of the experimental runs in this Laboratory, in which the equivalent length of straight pipe in pipe diameters is plotted against $\frac{D\,v\,s}{z}$. For reasons discussed in the next section, the resistance of the equivalent length of straight pipe was calculated from the recommended average line on Fig. 12, and not from the observed value in the simultaneous reading on the straight pipe in a particular experiment. A considerable proportion of the observed data had to be omitted from Fig. 11 to prevent the points from becoming crowded, but the points as given are strictly representative of all the results. In the lower turbulent flow region data are also added from other investigators which are quite consistent with the points determined by this Laboratory.

Of the points determined in this Laboratory, the results by Kite and Kennedy in 4-in. pipes at fairly high velocities appear to be distinctly lower than the results for 1-in. and 2-in. pipes, which agree very well. This effect is almost certainly due to the fact that the distance between the two elbows of the 4-in. line (see Fig. 2) was too small to permit the full disturbing influence of the first elbow to manifest itself, and the average pressure drop per elbow was therefore low, especially at high velocities, compared with that in 1-in. and 2-in. lines where the distance between the two elbows was comparatively large. This would also indicate that the resistance of a standard return bend would be distinctly less than that of two elbows placed some distance apart.

From a careful consideration of these results it appears to be fairly conclusive that the elbow correction, like f, is a function primarily of the modulus $\frac{D\,v\,s}{z}$. The rule of 30 pipe diameters per elbow appears to be about as good as can be derived for the entire region of turbulent flow. (The data, while apparently indicating the slight curvature as drawn, do not really justify anything more than a straight horizontal line.) However, Fig. 12 brings to light a hitherto unsuspected fact—namely, the existence of a sharp break in the correction curve at the critical velocity for commercial pipes beyond which, as $\frac{D\,v\,s}{z}$ decreases into the region of viscous flow, the magnitude of the correction rapidly grows less, apparently flattening off for very small values of $\frac{D\,v\,s}{z}$ to about 2 or 2.5 pipe diameters, which is little more than the actual length of the elbow itself.[20]

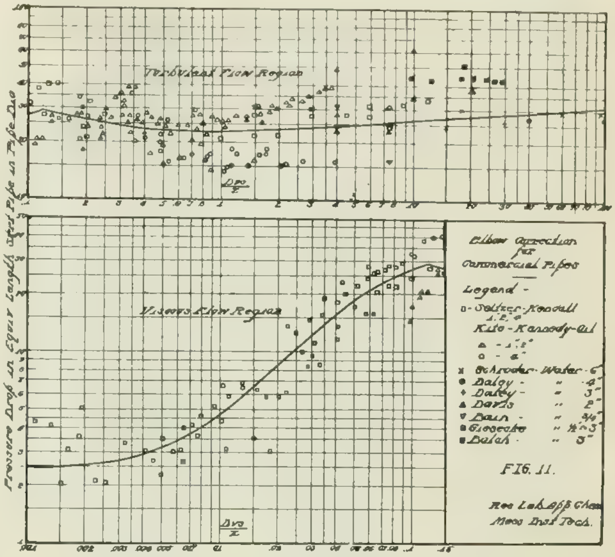

FIG. 11

1—Balch, University of Wisconsin, *Bull. Eng. Series*, **7**, No. 3, 253, Paper No. 578.
2—Giesecke, University of Texas, *Bull.* **1759** (Oct. 20, 1917).
3—Daly, Schoder and Bain, *Cornell Civil Eng.*, **20** (1911–12), 107.
4—Davis, University of Wisconsin, *Bull. Eng. Series*, **6**, No. 4, 115.

THEORETICAL ASPECTS OF THE RESULTS

In the course of evolving the method of presentation given in the previous sections and recommended for practical use in the following section, a number of interesting points of theoretical importance have come to light and seem to justify at least passing comment. In most cases they amount to alternative methods of presentation of the same results, which need not concern one interested merely in the practical aspects of the problem.

The preceding results show clearly that for a very wide range of conditions f is a function of $\frac{D\,v\,s}{z}$. What function?

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[20] The complete tabulated data on the 400 odd runs are obviously too bulky for reproduction, but are available for inspection at any time in the files of this Laboratory.

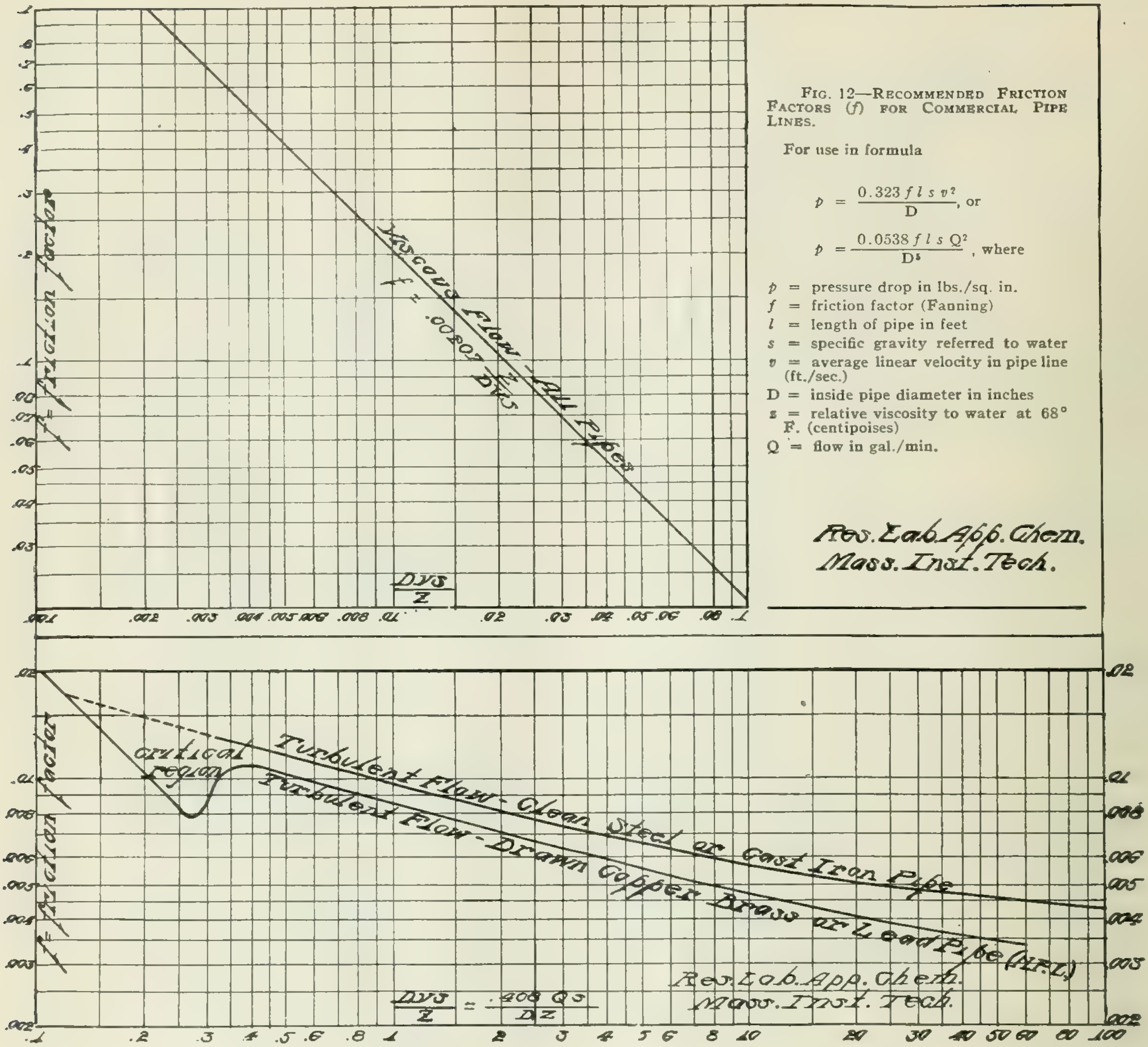

FIG. 12—RECOMMENDED FRICTION FACTORS (f) FOR COMMERCIAL PIPE LINES.

For use in formula

$$p = \frac{0.323\, f\, l\, s\, v^2}{D}, \text{ or}$$

$$p = \frac{0.0538\, f\, l\, s\, Q^2}{D^5}, \text{ where}$$

p = pressure drop in lbs./sq. in.
f = friction factor (Fanning)
l = length of pipe in feet
s = specific gravity referred to water
v = average linear velocity in pipe line (ft./sec.)
D = inside pipe diameter in inches
z = relative viscosity to water at 68° F. (centipoises)
Q = flow in gal./min.

This important point and its significance have scarcely been mentioned.

Referring to Fig. 12, since the line for the viscous flow region is straight and at an angle of 45° (slope = -1) it can readily be shown that its equation is

$$f = 0.00207\ \frac{z}{D\,v\,s}.$$

Substituting this value of f in Fanning's equation, it is possible to derive a general equation for flow for this region which is, as noted previously, simply the modified Poiseuille's equation,

$$p = \frac{0.000668\, z l v}{D^2}.$$

Deriving an equation for the curved line in the turbulent flow region is not, however, such a simple matter. The best form for the equation appears to be

$$f = a + b\left(\frac{D\ v\ s}{z}\right)^n.$$

where n is a negative exponent. Using this form of equation and deriving the constants, it is found that the best equation for turbulent flow in smooth pipes (as already worked out by Lees[21]) is:

$$f = 0.0018 + 0.00662\left(\frac{z}{D\,v\,s}\right)^{0.355}$$

Applying the same method to the recommended line for commercial pipe gives the new equation of the form:

$$f = 0.0035 + 0.00594\left(\frac{z}{D\,v\,s}\right)^{0.424}$$

Substituting the latter value of f in the Fanning equation gives as the most accurate *general* equation for turbulent flow in commercial pipes the following:

$$p = \frac{0.323\, l s v^2}{D}\left[0.0035 + 0.00594\left(\frac{z}{D\,v\,s}\right)^{0.424}\right]$$

A similar equation can readily be derived for turbulent flow in smooth pipes. It is obvious, however, that this equation is too complicated for any practical calculations—or indeed for giving a clear picture as to the comparative effects of the different variables. In order to secure such a semiquantitative visualization for the case of commercial pipes, it is possible to draw a straight line which is fairly representative of the turbulent flow curve for commercial pipes in Fig. 12, which has the equation:

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[21] *Proc. Roy. Soc. London*, **1914**, 406.

$$f = 0.01 \left(\frac{\mathrm{D}\, v\, s}{z} \right)^{0.2}$$

Substituting this value for f in the Fanning equation, we obtain

$$p = \frac{0.00323\, s^{0.8}\, z^{0.2}\, l\, v^{1.8}}{\mathrm{D}^{1.2}}$$

which is a reasonably accurate formula for the middle range of turbulent flow in commercial pipes. Actually, of course, the slope and the intercept of the curved line are continually changing, which changes the value of the constant in the above equation for f from 0.01 to 0.007, while the exponent varies from 0.13 to 0.26. This accounts for the fact that many investigators studying a comparatively narrow range of data have proposed formulas with fractional exponents similar to that given above, but each writer gives different values for the constant and for the exponent, depending on the particular part of the region and condition of pipe surface with which they were working. When working with water alone, as in most of the experiments, z and s have both been erroneously assumed to be constant and therefore became part of the proportionality constant.

There are also certain matters of interest in connection with the flow through elbows. As noted in that section, the resistance through an elbow was figured in terms of the equivalent resistance of straight pipe as *calculated* from the straight line in Fig. 12, rather than in terms of the resistance of a straight pipe as *measured* in the same run. This made little difference, except in the critical region, but when the equivalent length of pipe was figured in terms of the abnormally low resistances actually measured in this critical region, the points in this vicinity formed a sharp hump for values of $\frac{\mathrm{D}\, v\, s}{z}$ between 0.12 and 0.35, as compared with the smooth curve obtained when using the theoretical line as a basis. The latter method of presentation was not used merely on account of this fact, however, but because if the recommended line is used in making the calculations for the straight pipe, the elbow effect should also be figured in terms of that line. Furthermore, although in straight pipe there is unquestionably a tendency toward perpetuating viscous flow into the turbulent flow region, this unstable tendency is undoubtedly less pronounced during flow through an elbow and the pipe immediately beyond it, which will very probably force the liquid into turbulent motion. The method of presenting the results is therefore sound on theoretical grounds and confirms the belief that elbows tend to diminish the importance of the dip in the critical flow region.

Recommended Methods of Calculation

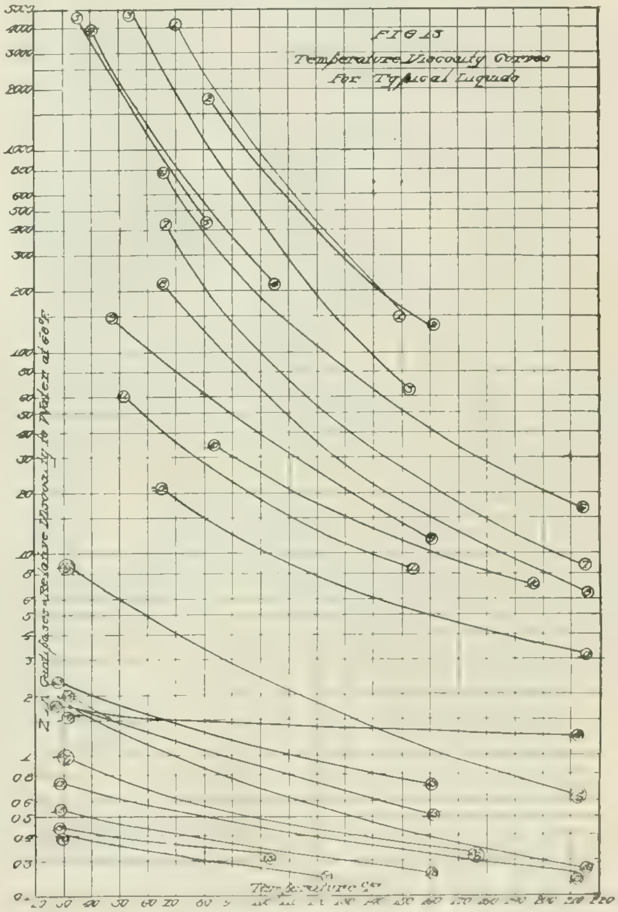
GENERAL PROCEDURE FOR CALCULATING PRESSURE DROP IN ANY PIPE LINE—With the data and charts previously presented, the calculation of the pressure drop through a pipe line under any specified set of conditions is a very simple matter. The steps involved may be outlined as follows:

1—Calculate the value of $\frac{\mathrm{D}\, v\, s}{z}$ (or its equivalent, $\frac{0.408\, \mathrm{Q}\, s}{\mathrm{D}\, z}$, if Q is known rather than v) for the fluid and pipe in question. If there is any uncertainty as to the measurement or estimation of any of the quantities, see the subsequent section on determination of the known quantities.

2—By referring to Fig. 12 find the value of f which corresponds to this value of $\frac{\mathrm{D}\, v\, s}{z}$, using the curve corresponding to the degree of roughness of the pipe in question. (See previous discussion of Fig. 12.) For values of $\frac{\mathrm{D}\, v\, s}{z}$ less than 0.002, extrapolations on the straight 45° line for viscous flow may readily be made by *dividing* the abscissae by 10 (or 100) and simultaneously *multiplying* the ordinates by 10 (or 100).

3—Using the same value of $\frac{\mathrm{D}\, v\, s}{z}$, refer to Fig. 11 for the equivalent length of straight pipe corresponding to each 90° elbow. Multiply this by the number of elbows, convert the correction from pipe diameters into feet, and add it to the length of straight pipe. (Note that two elbows very close together, or a return bend, have less effect than two elbows some distance apart.)

4—Insert this value of f in the modified Fanning equation, $p = \frac{0.323\, f\, l\, s\, v^2}{\mathrm{D}}$ or its equivalent, $p = \frac{0.0538\, f\, l\, s\, \mathrm{Q}^2}{\mathrm{D}^5}$, and obtain the pressure drop directly. *This method and this formula should be used regardless of whether the liquid is in viscous or turbulent motion.*



1—Mexican petroleum (Mex. Pet. Co.) (See Fig 5)
2—Meprolene (Parks-Cramer Co) (See Fig. 5)
3—Cal. heavy crude, 15.2° Bé. (Std. Oil Co.)
4—Castor oil (Smithsonian Tables)
5—Glycerol (Smithsonian Tables)
6—Mobiloil B (Vacuum Oil Co.)
7—Mobiloil A (Vacuum Oil Co.)
8—Texas engine oil (Vacuum Oil Co)
9—Olive oil (Smithsonian Tables)
10—Linseed oil (Smithsonian Tables)
11—Cal. light crude 24.4° Bé. (Std. Oil Co.)
12—Nonviscous neutral (Vacuum Oil Co.)
12A—Amyl alcohol (Opt inactive) (Smithsonian Tables)
13—Mercury (Smithsonian Tables)
14—Turpentine (Smithsonian Tables)
15—Ethyl alcohol (Smithsonian Tables)
16—Water (Smithsonian Tables)
16A—Benzene (Smithsonian Tables)
17—Octane (Smithsonian Tables)
18—Heptane (Smithsonian Tables)
19—Carbon disulfide (Smithsonian Tables)
20—Hexane (Smithsonian Tables)

GENERAL PROCEDURE FOR CALCULATING OTHER QUANTITIES—The foregoing procedure must, of course, be slightly modified in case the permissible or available pressure drop is known and it is desired to calculate any one of the other five quantities which may be unknown in a given practical problem. To anyone familiar with such calculations these modified methods are fairly obvious, but it will be helpful to those less familiar to suggest what appears to be the shortest way of arriving at the final results for each of the other cases.

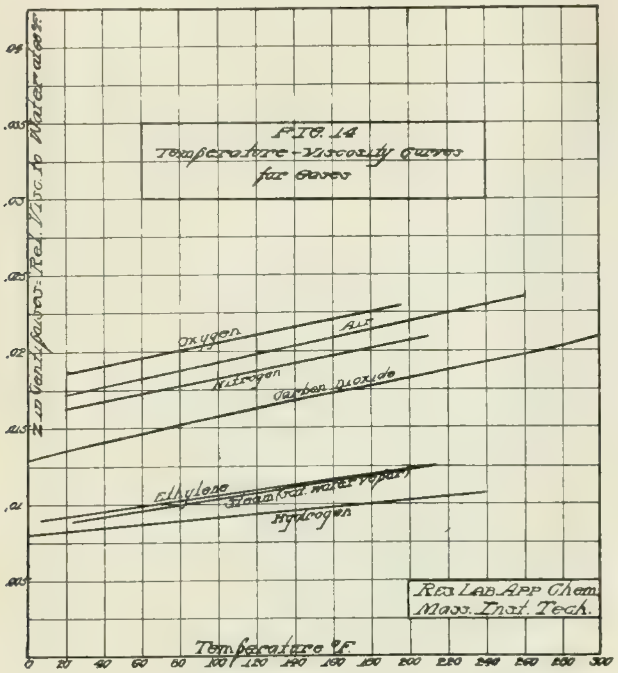


FIG. 14
Temperature-Viscosity Curves for Gases

1—If l is the unknown (which seldom happens) calculate exactly as described in the previous section, but transpose the Fanning equation so as to solve for l instead of p.

2—If z is the unknown (as when it is desired to know how hot an oil must be heated in order to give a specified discharge under definite conditions) calculate the permissible f from Fanning's equation (which does not involve the assumption of any value for z). Then find the value of $\frac{D v s}{z}$ in Fig. 12 which corresponds to this value of f, and solve this latter equality for z, which is the only unknown involved (neglecting small variations in s).

3—If D, v, or s is the unknown (the latter only in handling gases) the situation is somewhat more complicated, since these quantities appear both in the friction modulus $\frac{D v s}{z}$ and in Fanning's formula.

These cases may be treated by the customary method of trial and error used by hydraulic engineers, starting with a reasonable value for f, but experience with classes in chemical engineering indicates that for various reasons it is usually preferable to assume a value for the unknown and calculate the resulting pressure drop in the ordinary way. If this comes too high or too low, assume a new value for D, v, or s which will give more nearly the proper pressure drop. By remembering that, for a given Q, p varies inversely as the fourth or fifth power of the diameter, the correct solution can very quickly be obtained. If the first approximation indicates that the value is in the viscous flow region, the simplest way to solve for one of these three variables is to substitute the known quantities directly in Poiseuille's equation,

$$p = \frac{0.000668\ z\, l\, v}{D^2}$$

or its equivalent,

$$p = \frac{0.000273\ z\, l\, Q}{D^4}.$$

METHODS OF DETERMINING THE KNOWN FACTORS—Six separate variables—D, v, s, p, l, and z—are involved in making the foregoing calculations, five of which must be known in order to solve for the sixth. The determination of the precise values and proper units of these five known quantities sometimes involves difficulties, and it seems desirable to outline the best procedure for determining them in any given case, and to present certain data and conversion charts which will aid in the solution of practical problems.

Viscosity—For use throughout this paper viscosity, z, is expressed in centipoises, which may be more readily visualized as the viscosity relative to water at 68° F., at which temperature water has a viscosity of one centipoise. Data in literature are frequently expressed in poises; these results should be multiplied by 100 to give the viscosity in centipoises.

For many definite chemical compounds entirely satisfactory viscosity data are available in the literature, and data for a number of these and for some commercial oils are presented graphically in Fig. 13. For most commercial purposes, however, it is desirable to make an independent determination of the viscosity of the fluid. To determine this directly in absolute units is difficult and time consuming, but it is possible, for liquids that are distinctly more viscous than water, to employ one of the standard instruments familiar in the oil trade, such as the Saybolt Universal viscosimeter, which measures the time of efflux of a given volume of liquid. For reasons discussed in several papers by the Bureau of Standards, this does *not* measure the true viscosity directly and is not applicable to liquids having a viscosity near that of water, but by the use of the conversion charts presented in Fig. 15[22] it is possible to determine the

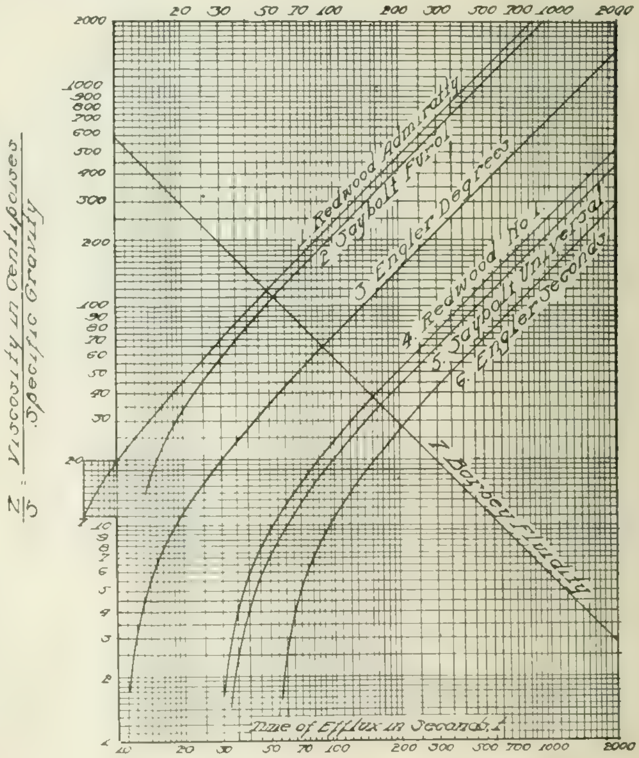


FIG. 15—CONVERSION DIAGRAM FOR VISCOSIMETERS

NOTE: For line 3, Abscissa, scale gives 10 × Engler degrees = 10(t/52).
For line 7, Time, t = 600, and scale gives flow in cc./hr.

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[22] Modified slightly from a chart drawn up by W. H. Herschel (Bureau of Standards). Method due to N. MacCoull, of the Texas Co.

correct value of $\frac{z}{s}$ from the readings on any standardized type of viscosimeter. The reciprocal of this ratio may be inserted directly into the expression $\frac{D\,v\,s}{z}$, or if z alone is desired it can readily be obtained by multiplying this ratio by s, the specific gravity of the liquid at the temperature in question.

Since the same method of calculation is applicable to most problems involving the flow of gases, data are also appended (Fig. 14) for a number of common gases, including steam. It will be noted that whereas the viscosity of liquids decreases rapidly with increase in temperature, the viscosity of gases *increases*. It is also important to remember that the viscosity of gases is practically independent of the *pressure*, though of course the latter factor does affect the density, s, in direct proportion, and hence changes the value of $\frac{D\,v\,s}{z}$, as would be expected.

It will be noted that the viscosities of the gases are far lower than those of the liquids, but it so happens that the effect is roughly counterbalanced by other factors—particularly their lower density—so that the values of $\frac{D\,v\,s}{z}$ used in handling gases commercially are not far distant from those most used in the flow of liquids.

It will be noted that the data on the viscosity of various fluids are plotted on semi-logarithmic paper, which tends to give rather flat curves and makes it possible to present data on liquids whose viscosities vary greatly and yet get equal percentage accuracy in all parts of the plot. For purposes of extrapolation or of interpolation from two observed points it is preferable to use a method of plotting which gives still flatter curves, and the one which the authors recommend[23] for this purpose is to plot the fluidity (the reciprocal of the viscosity) against the temperature on an ordinary scale. Most oils give nearly a straight line on this type of plot, unless they approach the point where paraffin begins to separate out or other disturbing factors enter into the determination.

Specific Gravity—The value of the specific gravity, s, must be expressed in units relative to water at 39° F. (temperature of maximum density). In other words, it is equivalent to the true density in grams per cc. Specific gravity figures are frequently given relative to water at some other temperature than 39° F. (4° C.) and hence are subject to some slight correction to give the proper value of s for use in the foregoing equations.

To convert Baumé readings to specific gravity use the formula $s = \frac{140}{130 + \text{Bé.}}$[24] for liquids lighter than water.

For convenience, Fig. 16 gives typical density curves for various liquids as a function of temperature, and Fig. 17 gives the same data for the commoner gases. In dealing with gases, care should be taken to use an *average* value if the pressure drop through the line is enough to cause appreciable variations in this factor.

Length of Pipe—This is, of course, measured in feet and the only precaution to be observed is to add to the actual length the equivalent length of pipe due to elbows, as found by using Fig. 11. For pipes less than 500 diameters long consideration must be given to entrance and exit losses, as pointed out later under "limitations."

Velocity—Velocity should be expressed in ft. per sec., and means the effective average velocity in the pipe, obtained by dividing the rate of discharge in cu. ft. per sec. by the cross-sectional area of the pipe in sq. ft. Data may be transposed from gal. per min. to velocity in ft. per sec., or vice versa, by the conversion formula, $v = \frac{0.408\ Q}{D^2}$. It is also possible to use another form of Fanning's equation, which involves Q instead of v if any considerable number of calculations have to be made on this basis. In this case, instead of $\frac{D\,v\,s}{z}$, it is necessary to calculate $\frac{0.408\ Q\,s}{D\,z}$ and to substitute the resulting value of f from Fig. 12 in the equation

$$p = \frac{0.0538\ f\,l\,s\,Q^2}{D^5}.$$

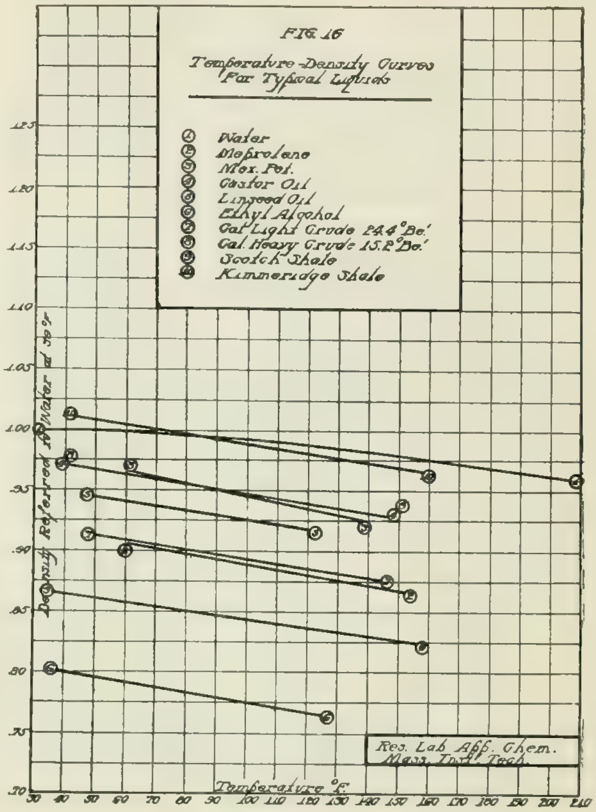

FIG 16

Temperature-Density Curves For Typical Liquids

Pipe Diameter—The inside pipe diameter used in this equation should be measured in inches. The nominal diam-

TABLE II—DIAMETER FUNCTIONS OF STANDARD IRON AND STEEL PIPE

Nominal Diameter In.	D Actual Inside Diameter In.	D^2	D^4	D^5	Actual Internal Cross-section Area Sq. In.
0.5	0.622	0.3869	0.1497	0.09310	0.3039
0.75	0.824	0.6790	0.4610	0.3799	0.5333
1.0	1.049	1.100	1.211	1.270	0.8639
1.5	1.610	2.592	6.719	10.82	2.036
2.0	2.067	4.272	18.25	37.73	3.356
2.5	2.469	6.096	37.16	91.75	4.786
3.0	3.068	9.413	88.60	271.8	7.392
4.0	4.026	16.21	262.7	1058.0	12.73
6.0	6.065	36.78	1353.0	8206.0	28.89
8.0	8.071	65.14	4243.0	34250.0	51.15
8.0	7.981	63.70	4057.0	32380.0	50.02
10.0	10.192	103.8	10790.0	109980.0	81.55
10.0	10.136	102.7	10560.0	106990.0	80.75
10.0	10.020	100.4	10080.0	101000.0	78.82
12.0	12.090	145.9	21370.0	258300.0	114.80
12.0	12.000	144.0	20736.0	248800.0	113.10
14.0	13.250	175.5	30750.0	407500.0	137.7
16.0	15.250	232.5	54200.0	825100.0	182.7
18.0	17.250	297.2	88500.0	1526000.0	224.0
20.0	19.250	370.5	137300.0	2640000.0	291.1
24.0	23.250	540.0	291900.0	6777000.0	424.5

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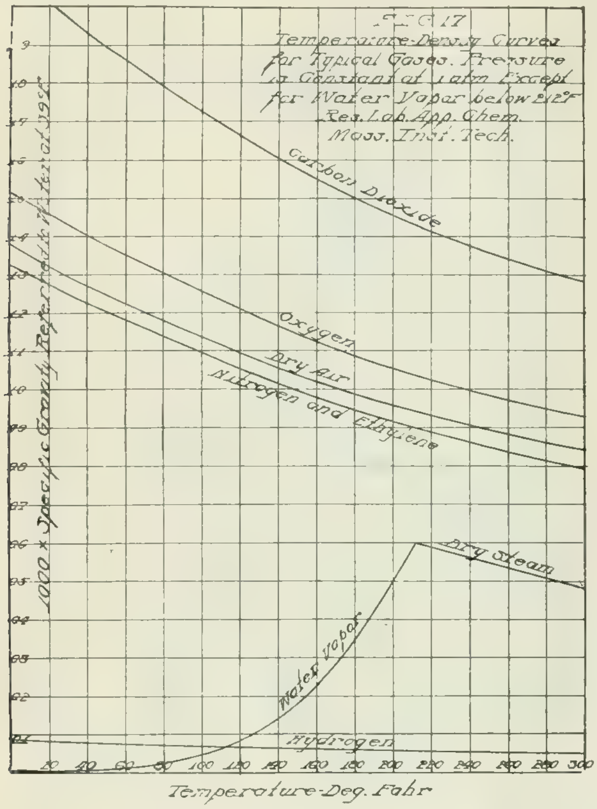
[23] More exact methods have been proposed, but are too complicated for most practical purposes.

[24] While this is the official B. of S. Baumé scale, the great bulk of the oil trade uses instruments calibrated on a scale which gives 141.5 instead of 140 for this figure.

eters used to identify commercial pipes do not correspond to actual inside diameters, but their exact dimensions have been quite well standardized within recent years, and the accepted figures for each nominal size of pipe are given in Table II. For precise work the diameters should be measured accurately, as this factor enters to the fourth or fifth power in some of the equations used.



Pressure Drop—The pressure drop should be expressed in lbs. per sq. in. If the data are given in any other form they may be converted by the use of Table III. If it is desired to calculate the theoretical horse power required, the following formula can be used:

$$\text{H. p.} = \frac{19.2 \times \text{gal./min.} \times \text{press. drop in lbs./sq. in.}}{33{,}000}$$

The actual horse power required equals this figure divided by the efficiency of the pump as a whole.

TABLE III

x	To Convert x to Lbs./Sq. In. Multiply by	To Convert Lbs./Sq. In. to x Multiply by
Lbs./sq. ft.	0.00695	144.
Cm. mercury	0.1934	5.171
Atmospheres	14.70	0.06804
Liquid head expressed in ft.[1]	0.4332 s	$\frac{2.309}{s}$

[1] This equals pressure drop in lbs. per sq. ft. divided by the liquid density at that point, which = 62.3 s.

LIMITATIONS TO APPLICATION OF RECOMMENDED METHOD OF CALCULATION—The data and methods of calculation given in this article cover substantially the entire field of the flow of all fluids, including gases and dry vapors, through commercial pipe lines. There are, however, a few exceptions which should be carefully noted before attempting to use the formula in certain special cases. These may be specified as follows:

1—The method is not directly applicable to the flow of *gases* where the drop in pressure along the pipe line is more than 10 or 15 per cent of the final *absolute* pressure, because the density and velocity of the fluid are thereby changed. If, however, *average* values are used for the density and velocity, instead of the initial or final values, this formula may be used for pressure drops up to 40 or 50 per cent without serious error. To make calculations for compressed air lines with still larger drops in pressure, it is necessary to use an approximate integrated form of the equation, which has previously been discussed by Lewis.[25] The regular method of calculation may, however, be used for all ordinary problems of handling air through circular ducts or steam in pipes lines.

2—The method is not applicable to flow through short sections of pipe opening into large chambers where the entrance and exit losses are appreciable in comparison with the friction losses through the pipe. These losses become inappreciable when the pipe is more than 1000 diameters long, and may generally be neglected for approximate calculations for lines longer than 300 diameters. For shorter tubes the reader is referred to the recent comprehensive treatment of Herschel.[26]

3—The method is not applicable to the flow of semisolid plastic materials, such as asphalt, clay suspensions, very viscous colloidal solutions, etc., where the laws of flow are modified by the tendency of the material to behave like a solid under certain conditions.

4—Precautions must be observed, and highly accurate results cannot be expected in cases: (*a*) where the pipe is badly corroded or tuberculated, and the apparent value of f may increase to double that given in the formula, owing partly to a decrease in the effective cross-sectional area; (*b*) where a hot oil is passing through a pipe line in straight line flow, and the existence of a large temperature gradient from the inside to the outside makes accurate calculations practically impossible; and (*c*) where there is any tendency to precipitate out solids (such as paraffin wax) on the walls or in the bottom of the pipe lines.

With these exceptions it is believed that the recommended method of calculation is applicable to an entirely satisfactory degree of accuracy to all commercial problems involving the flow of fluids through pipe lines.

ILLUSTRATIVE EXAMPLES

To illustrate the practical utilization of the foregoing charts and tables, two typical examples are appended herewith.

EXAMPLE 1—CALCULATION OF REQUIRED PRESSURE DROP

It is desired to transmit 20 U. S. gal. per min. (686 oil bbls. per 24 hrs., based on 1 oil bbl. = 42 U. S. gal.) of a very viscous oil at 70° F. through a standard 6-in. steel pipe line. What will be the pressure drop as lbs. per sq. in. per mi.?

DATA—The oil at 70° F. has a time of 9050 sec. in a Saybolt Universal viscosimeter and a gravity corresponding to 15.2° Bé.

SOLUTION—From Table II, one sees that $D = 6.07$ in. and $D^2 = 36.78$.

Since the average velocity $= \frac{0.408\,Q}{D^2}$, $v = \frac{0.408 \times 20}{36.78} = 0.222$ ft. per sec.

From Fig. 15 it is seen that the value of $\frac{z}{s}$, corresponding to a time of 9050 Saybolt sec., is 1990.

Hence the numerical value of

$$\frac{D\,v\,s}{z} = \frac{6.07 \times 0.222}{1990} = 0.000677,$$

and the value of f corresponding (Fig. 12) is 3.06 (extrapolation made by multiplying ordinate and dividing abscissae scales by 10).

The specific gravity at 70° F. $= \frac{140}{130 + 15.2} = 0.964.$

The value of p is figured from the modified Fanning equation:

$$p = \frac{0.323\,f\,l\,s\,v^2}{D} = \frac{0.323 \times 3.06 \times 5.280 \times 0.964 \times 0.222^2}{6.07}$$

$$= 40.8 \text{ lbs. per sq. in.}$$

Thus it is found that this oil flowing at an average velocity of 0.222 ft. per sec. gives a pressure drop of 41 lbs. per sq. in. per mi.

EXAMPLE 2—CALCULATION OF DIAMETER REQUIRED

Dry compressed air at 80° F. must be delivered through 200 ft. of straight steel pipe connected by means of three standard elbows at a rate equivalent to 1000 cu. ft. of "free" air per min. The initial air is at a pressure of 150 lbs. per sq. in. What size of standard steel pipe must be used in order that the drop in pressure shall not exceed 10 lbs. per sq. in.?

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[25] THIS JOURNAL, **8** (1916), 1133.

[26] "The Flow of Liquids through Short Tubes," *Proc. Am. Soc. Civil Eng.*, **84** (1921), 527.

Solution—From Fig. 14, $z = 0.0188$ at 80° F.

From Fig. 17, $z = 0.00118$ at 80° F. and 1 atm. Since the average pressure is $\frac{150 + 140}{2 \times 14.7} = 9.87$ atm., $s = 9.87 \times 0.00118 = 0.01165$.

Since free air refers to air at 1 atm. and 70° F. the actual volume at 80° F. (540° F. absolute) and 9.87 atm. pressure is

$$\frac{1000 \times 540}{9.87 \times 530} = 103.2 \text{ cu. ft. per min.,}$$

and $v = \frac{103.2 \times 144}{60 \times 0.785\, D^2} = \frac{315}{D^2}$ ft. per sec. at 80° F. and a mean pressure of 9.87 atm.

$$\text{Then } \frac{D\, v\, s}{z} = \frac{D \times \frac{315}{D^2} \times 0.01165}{0.0188} = \frac{195}{D}. \qquad (a)$$

Taking the equivalent length of each elbow as 30 pipe diameters,

$$l = 200 + \frac{3 \times 30\, D}{12} = 200 + 7.5\, D.$$

$$\text{But } p = \frac{0.323\, f\, l\, s\, v^2}{D},$$

$$\text{so } p = \frac{0.323\, f[200 + 7.5\, D]\, 0.01165 \times (315)^2}{D^5}$$

$$p = \frac{374\; f[200 + 7.5\, D]}{D^5} = \frac{\text{Lbs.}}{\text{Sq. in.}}. \qquad (b)$$

As noted above, one may assume a value of D *actually obtainable*, find from Fig 12 the corresponding value of $\frac{D\, v\, s}{z}$, and calculate p. The result of such procedure is shown below.

Nominal Dia.	Actual Dia. (D)	$\frac{D\, v\, s}{z}$ (From Eq. a)	f (From Fig. 12)	D^5 (Table II)	p (From Eq. b)
1.5	1.61	121[1]	0.0041	10.82	30.1
2	2.07	94.3	0.0043	37.7	9.2

[1] The friction factor for this case was taken from Fig. 10, as Fig. 12 does not show f for values of $\frac{D\, v\, s}{z}$ beyond 100.

It should be noted that although the first trial diameter (1.61 in.) called for a pressure drop of 30 lbs. per sq. in., a diameter only slightly larger (2.07 in.) gave practically the desired pressure drop. This is because p varies inversely as the *fifth* power of diameter. Hence a 2-in standard steel pipe must be used to meet the specified conditions.

Acknowledgment

In conclusion the writers desire to express their appreciation of the many helpful suggestions of Dr. W. K. Lewis, at whose instigation this work was first undertaken; of the accurate work of Mr. V. V. Kendall, who aided in the conduction and direction of much of the experimental work; and of that of Messrs. Kite and Kennedy, who made the runs in the turbulent and critical flow regions. Acknowledgments are also due to the various coöperating companies mentioned in the introduction; and to Mr. R. S. Danforth of The Kinney Manufacturing Company, and Dr. W. H. Herschel of the Bureau of Standards, for valuable suggestions.

The Determination of Carbon Dioxide in Baking Powder[1,2]

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The gasometric method for the determination of carbon dioxide in baking powder is as accurate as the absorption methods. It is much more rapid and requires but a single piece of apparatus. It can be used for the determination of both total and residual carbon dioxide.

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At the 1920 meeting of the Association of Official Agricultural Chemists the senior author suggested, as a substitute for the present official methods for determining total carbon dioxide in baking powder, a modification of the gasometric method originally devised by Van Slyke for the determination of carbon dioxide in blood plasma.[4]

Its use has since been extended to the estimation of residual carbon dioxide. The object of the present paper is to describe this procedure and report the results obtained with it.

Procedure

TOTAL CARBON DIOXIDE—The procedure for the determination of total carbon dioxide in baking powder is identical with that for the analysis of marl and limestone as given in the original description of the method, except that 100-mg. samples are used.

RESIDUAL CARBON DIOXIDE—A 2-g. sample of the well-mixed material is weighed into a small beaker and 20 cc. of distilled water are added. The mixture is thoroughly stirred, allowed to stand for 20 min. at room temperature, and set in a bath of boiling water for the same length of time. Finally it is boiled for 1 min. The addition of a drop or two of octyl alcohol to reduce foaming is sometimes advisable at this point. One sample is diluted to 25 cc. in a volumetric flask, and 1-cc. samples are used for the determination.

The accompanying table shows the results obtained with this method and with the two official methods. They are typical of the agreement of results which have been obtained in this laboratory with all sorts of carbonates during the past year.

Comparison of Official and Gasometric Methods for Determining Carbon Dioxide in Baking Powder

Total Carbon Dioxide

	I*a* (CaCO$_3$)	II*a*	III*a*	IV*a*	V*a*
Official method	43.34	13.54	13.48	16.73	14.62
	43.81	13.29	13.11	17.03	14.35
	43.70	13.30	13.48	16.90	14.29
Gasometric	43.78	13.55	13.34	17.03	14.52
	43.70	13.52	13.31	16.89	14.52
	43.78	13.52	13.29	16.92	14.53

Residual Carbon Dioxide

	I*b*	II*b*	III*b*	IV*b*	V*b*
Official method, Heidenhain	0.73	1.15	1.74	5.51	1.27
Knorr	0.85	1.26	1.51	5.26	1.39
Gasometric	0.75	1.16	1.63	5.45	1.35
	0.75	1.31	1.59	5.62	1.27

In order to test the method when a product contained a water-insoluble carbonate, Sample IV*b* was made up by mixing Sample V*b* and calcium carbonate. Duplicate results agreed as closely as did those with other products.

Only one source of trouble has been encountered. It has been found necessary to lubricate the stopcocks of the apparatus rather frequently with a heavy grease to prevent leakage during the maintenance of the high vacuum used. If the carbon dioxide is absorbed each time and the residual air measured instead of being calculated from the table, this source of error is avoided. With proper attention to stopcocks, however, this is unnecessary.

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[1] Received November 3, 1921.

[2] Published as Journal Article No. 20 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

[3] Research Associate in Chemistry.

[4] *J. Biol. Chem.*, **30** (1917), 347; *Soil Sci.*, **10** (1920), 41.

Phthalic Anhydride. V—The Preparation of Phthalic Anhydride by the Catalysis of the Vapor Phase Reaction between Naphthalene and Atmospheric Air[1,2]

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So far as revealed by the literature, phthalic acid and phthalic anhydride always have been prepared on a commercial scale by the oxidation of naphthalene or some of its simpler derivatives. In the methods used up to the last few years of the nineteenth century comparatively expensive chemicals, such as nitric acid or chromic acid, were used as the oxidizing agents.[3] During the last decade of the nineteenth century the growing demand for phthalic anhydride for use in the preparation of xanthene and the indigoid dyes led to research toward the discovery of cheaper processes for its manufacture. A method for converting naphthalene to phthalic anhydride, using sulfuric acid as the oxidizing agent in the presence of a mercury salt as a catalyst, was discovered by E. Sapper, and was patented by the Badische Anilin und Soda Fabrik[4] in 1896. From then until now this process has been commonly described as the commercial method for making phthalic anhydride. It is said to have been employed on an enormous scale by the Badische Anilin und Soda Fabrik in connection with their manufacture of synthetic indigo, and it is interesting to note that the present contact process for producing sulfuric acid is a result of efforts to utilize the sulfur dioxide formed during the process.[5]

When importations of phthalic anhydride from Germany were interrupted during the war, many attempts were made in this country to prepare phthalic anhydride by this sulfuric acid oxidation process as described in the patents and in chemical literature. The difficulties discovered in its application and the disappointing yields resulting from its use have been mentioned by Gibbs.[6] Even when most successfully put into practice, the method is unsuitable for small-scale operation. The large quantities of sulfur dioxide evolved create a nuisance or must be converted into sulfur trioxide by means of expensive apparatus.

Other processes for the manufacture of phthalic anhydride have been patented or described in the literature in recent years by Prochazka,[7] Imray,[8] Ditz,[9] and others,[10] while improvements on the sulfuric acid and mercury process have been patented by Greenley[11] and Takahaski.[12] So far as known these processes have not been found in practice to have any great advantage over the older sulfuric acid process.

In studying the sulfuric acid oxidation process, the writers soon realized its many disadvantages, and, of other possible methods, it was concluded that the direct oxidation of naphthalene with air in the presence of a catalyst, if feasible, would be ideal in simplicity and cheapness. The possibility of the successful development of a process of this nature was suggested by the oxidation of toluene to benzaldehyde and benzoic acid with air in the presence of catalysts, which had been successfully carried out by Gibbs.[6] Vanadium pentoxide and molybdenum trioxide had been found to be the best catalysts in this process.

In the first attempts to prepare phthalic anhydride by the catalytic oxidation of naphthalene in the gas phase, a crude form of apparatus was assembled which permitted the mixing of naphthalene vapor with oxygen or air in approximately known proportions and bringing the mixed gases in contact with the catalyst at temperatures up to about 500°. The temperatures were measured roughly. In the few experiments where oxygen was used it was found that with vanadium pentoxide at temperatures around 275° and with molybdenum trioxide at temperatures around 325° there was some darkening of the naphthalene which condensed, some formation of carbon dioxide, and some development of acidity. But if the temperature rose above 300°, in the case of vanadium pentoxide, or 350°, in the case of molybdenum trioxide, ignition of the naphthalene vapor took place, sometimes with violent explosions. If the temperature was kept at a safe point the development of acid was very slight. When air was substituted for oxygen it was found that the temperature could be raised to nearly 500° without ignition of the vapors and that at these higher temperatures the product condensed contained considerable quantities of acid. It was demonstrated that phthalic anhydride was present in this condensate.

COMPARISON OF CATALYTIC EFFECT OF VARIOUS SUBSTANCES FOR CONVERSION OF NAPHTHALENE TO PHTHALIC ANHYDRIDE

PLAN OF TESTS—Since it had been shown that naphthalene was converted to phthalic anhydride when naphthalene vapor and air were brought into contact with certain catalysts at temperatures above 350°, it was planned to test each of a number of possible catalysts under fairly uniform conditions in order to discover the substance most suitable for the catalysis of this reaction. It was planned to mix a known weight of naphthalene vapor with a known volume of air, to keep the two gases in proportions practically the same as those required by theory for the oxidation of naphthalene to phthalic anhydride, to carry out the reaction at the highest temperature which could be maintained without ignition, to condense all the solid and liquid products of the reaction, and to determine the total acid formed and the total naphthalene recovered.

Since the object of the experiments was to develop a practical process for the manufacture of phthalic anhydride rather than to study the catalytic action of the substances

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[1] Received September 28, 1921.

[2] Published as Contribution No. 53 from the Color Laboratory of the Bureau of Chemistry, U. S. Department of Agriculture.

[3] H. Luddens, *Chem.-Ztg.*, **15** (1891), 585; *J. Soc. Chem. Ind.*, **10** (1891), 758.

[4] D. R. P. 91,202 (1896); Brit. Patent 18,221 (1896). See *Chem. Zentr.*, **68** (1897), I, 1040; *J. Soc. Chem. Ind.*, **16** (1897), 676.

[5] "The History of the Development of the Manufacture of Indigo." Lecture delivered by Brunck on the dedication of the Hofmann Memorial in Berlin, October 20, 1900.

[6] "Phthalic Anhydride. I—Introduction," THIS JOURNAL, **11** (1919), 1031.

[7] *Ber.*, **30** (1897), 3108. Naphthalene is oxidized to phthalic acid by means of permanganate in boiling water.

[8] Brit. Patent 15,527 (1901). Naphthols and other naphthalene derivatives are oxidized to phthalic acid by heating in alkaline solution with various metallic oxides or peroxides. The same processes are described in D. R. P. 138,790 (1903), 139,956 (1903), and 140,999 (1903). A similar process is described in D. R. P. 136,410 (1902). See *J. Chem. Soc. (Abstr.)*, **84** (1903), 487, 561; *J. Soc. Chem. Ind.*, **20** (1901), 1139; *Chem. Zentr.*, **73** (1902), II, 1371; **74** (1903), II, 1106.

[9] *Chem.-Ztg.*, **29** (1905), 581; *J. Chem. Soc. (Abstr.)*, **88** (1905), 516. Naphthalene is oxidized by sulfuric acid in the presence of salts of the rare earths, mainly Ce salts. The process is described in D. R. P. 158,609 (1905). See *Chem. Zentr.*, **76** (1905), I, 841.

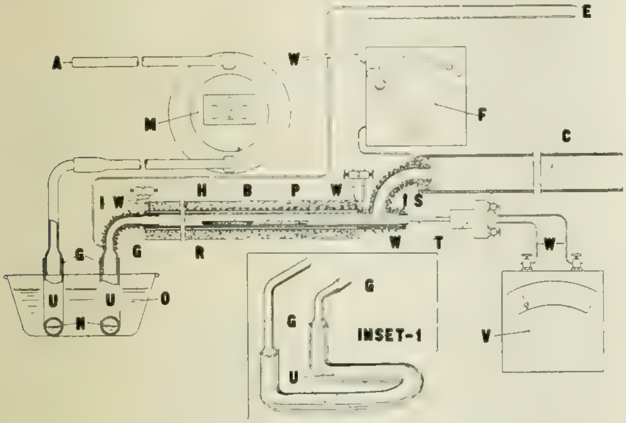
[10] D. R. P. 152,063 (1904). Naphthalene is oxidized electrolytically to naphthoquinones or phthalic acid in an acid solution, using a Ce salt as a catalyst.

[11] U. S. Patent 1,261,022 (1918); *C. A.*, **12** (1918), 1558.

[12] Jap. Patent 31,387 (1917); *C. A.*, **12** (1918), 157.

as a matter of scientific interest, no great care was taken to prepare absolutely pure chemical compounds for use as catalysts, to attain any great precision in quantitative measurements, or to hold the conditions under which the experiments were made absolutely uniform in the different tests.

PREPARATION OF CATALYSTS—Most of the substances selected as possible catalysts were metallic oxides. Oxides, such as those of arsenic, antimony, lead, and zinc, which might volatilize or form volatile products under the condition of the experiment, were believed to be impracticable and were not tested. The state of oxidation of the metallic oxides selected for testing was felt to be of little importance, since the final state of oxidation undoubtedly would depend upon the conditions of the experiment.



The metallic oxides were in some cases purchased as such. Several were prepared by igniting nitrates of the metals, and a few from other salts by common methods. Vanadium pentoxide was made by heating ammonium metavanadate at about 200° until the hot material no longer smelled of ammonia. Chromium sesquioxide and manganese sesquioxide were prepared from chromium trioxide and manganese dioxide, respectively, by heating these oxides to low redness and adding naphthalene in small portions to the hot material until there was no ignition. Platinum was deposited in a finely divided form upon magnesium oxide by mixing solutions of platinum chloride and magnesium nitrate, evaporating the mixture to dryness, igniting the residue, treating the product with ammonia water, drying, and igniting again. The product contained about 5 per cent of platinum.

Some of these catalysts were prepared from chemicals supposed to be of the very highest purity, but most of them were made from C. P. chemicals which had been examined and passed as suitable for use as analytical reagents.

APPARATUS—A great deal of trouble was experienced in discovering a form of apparatus which would permit the desired control of conditions and measurements of results, and which would endure the temperature desired. The form finally developed is shown in the figure. Apparatus of this general form was used not only for this series of experiments but for numerous others in connection with the development of the process described in this paper. It was found to be of fairly general application in making tests of catalytic gas-phase reactions.

A is the air supply and M is a dry gas meter which measures the air. In U the naphthalene is volatilized and the vapor mixed with air. It is a U-tube with the ends bent at right angles to the plane of the U so that it will lie on the bottom of the oil bath O, with the ends of the tube above the surface of the oil. Its form can be seen in the inset. Outlet and inlet tubes are fitted into it with ground-glass joints, G. The tube is of Pyrex glass and has an inside diameter of about 2 cm. It is charged with naphthalene, N, in such quantity that the portion of the tube lying on the bottom of the oil bath is not quite filled. Hence the air passes over the melted naphthalene but does not bubble through it.

The outlet of the U-tube is covered with a thin sheet of asbestos, I, and is heated with a few turns of resistance wire, W, so that it will not be closed by the solidification of naphthalene on the walls. This outlet is connected to the reaction tube R by a ground-glass joint, G.

The reaction tube R is made of Pyrex glass. It is 65 cm. in length and has an inside diameter of about 2 cm. It branches at the rear end, a thermocouple being inserted through the straight branch while the effluent gases are led off through the side branch. The catalyst is placed in the reaction tube in porcelain combustion boats, B, which are about 75 mm. long, 15 mm. wide, and 8 mm. high.

The condenser C is simply an air-cooled glass tube of about 5 cm. inside diameter. A tube of this diameter and about 80 cm. long, with a plug of cotton wool in the open end, was found adequate to collect all visible solid reaction products when the production of phthalic anhydride was high. In other cases two connected tubes with a total length of 175 cm. were used. The condenser C is fitted on to the reaction tube R by means of a built-up asbestos stopper.

The reaction tube R lies in a copper heating tube, H, which is heated by the resistance wire W. The copper tube is covered with a thin layer of sheet asbestos, the resistance wire is wound upon this, and the whole is heavily insulated with asbestos. The current which heats tube H also passes through sections of resistance wire wound upon the outlet of tube U and upon the side branch of the reaction tube. These sections of resistance wire are connected by means of binding posts, so that the connections can be broken readily. This allows the reaction tube to be withdrawn from the heating tube and the U-tube to be disconnected from the reaction tube. The current is controlled by the resistance F.

The temperature of the reaction tube at the point P is measured by means of a platinum-rhodium thermocouple, T. The wires of the thermocouple are inserted in a special protecting tube made of Pyrex glass.

CONTROL OF GAS MIXTURE—It was thought that the proportion of naphthalene vapor in the gas mixture could be controlled simply by controlling the temperature of the bath in which the U-tube rested. It was found, however, that the quantity of naphthalene carried out of the U-tube depended not only upon the temperature of the bath but also on several other conditions, such as the temperature of the parts of the tube above the surface of the oil and the velocity of the air through the tube. At a given temperature in the bath a rapid stream of air would emerge from the U-tube, containing a greater proportion of naphthalene than would a slowly moving stream of air. Since all the conditions involved could not be controlled easily it was difficult in all experiments to keep the ratio of naphthalene vapor to air as nearly constant as was desired.

ANALYTICAL PROCEDURE—Before and after each experiment the U-tube was wiped free from oil, washed with a cloth saturated with ether, and, after standing for a few minutes in the air, was weighed on an analytical balance, the weight being recorded to the nearest centigram. The major part of the product in the condenser was scraped out and placed in a desiccator. The product remaining in the condenser was rinsed out with ether into a small weighed beaker. This beaker was placed in a vacuum desiccator where the ether was evaporated by directing upon its surface a rapid stream of air which had been dried by passing through sulfuric acid. In this way the ether could be evaporated without condensation of moisture on the beaker and in the residue. The beaker

Table I—Tests of Various Substances as Catalysts for the Conversion of Naphthalene to Phthalic Anhydride

Expt. No.	Substance Tested	Vol. Air per 1 G. Naphthalene Liter	Time of Contact Sec.	Specific Time of Contact	Temperature °C.	Naphthalene Converted Per cent	Naphthalene Recoverable Per cent	Naphthalene Lost Per cent	Anhydride Produced per Hr. Gram	Acid in Product as Anhydride Per cent	Yield of Anhydride on Naphthalene Attacked Per cent
256	MgO	5.1	4.06	2.65	413	Trace	84.6	15.4	Trace	Trace	..
434	Al_2O_3	4.3	2.39	2.39	400	0.2	56.1	43.7	0.013	0.1	0.1
258	SiO_2	4.2	3.72	2.43	397	0.1	78.9	21.0	0.007	0.2	0.6
411	TiO_2	5.1	2.57	2.57	419	0.3	57.8	41.9	0.009	0.5	0.6
188	ZrO_2	3.9	2.03	2.21	450	0.2	51.2	48.6	0.019	0.6	0.6
183	CeO_2	3.2	1.96	2.14	455	0.2	61.1	38.7	0.017	0.4	0.5
197	V_2O_5	4.7	2.44	2.66	450	3.7	42.9	53.4	0.191	9.4	7.5
189	Co_2O_5	4.1	2.02	2.20	455	0.3	89.6	10.1	0.025	0.5	3.9
432	Cr_2O_3	4.0	2.45	2.45	401	Trace	52.5	47.5	Trace	Trace	..
271	MoO_3	4.5	2.90	1.85	426	10.2	62.2	27.6	0.590	16.2	31.1
182	WO_3	3.6	2.01	2.19	428	2.7	63.0	34.3	0.226	4.9	8.6
415	UO_3	5.2	2.73	2.73	427	1.3	47.3	51.4	0.049	3.3	3.0
278	Mn_2O_3	4.8	3.87	2.54	401	1.8	46.0	52.2	0.100	4.3	3.8
181	Fe_2O_3	3.2	1.97	2.15	456	0.3	64.8	34.9	0.020	0.4	0.7
184	NiO	5.2	1.97	2.15	455	0.2	51.7	48.1	0.019	0.5	0.5
416	Co_2O_3	4.5	2.67	2.67	410	0.1	21.5	78.4	0.005	0.6	0.2
187	Cu_2O	5.0	2.13	2.32	445	0.5	35.7	63.8	0.024	1.4	0.8
184	5% Pt; 95% MgO	5.1	2.20	2.40	431	0.2	43.8	56.0	0.009	0.4	0.3

and residue were further dried for several hours in a desiccator over sulfuric acid. The quantity of ether used was noted. The amount of naphthalene lost during the evaporation of a known quantity of ether by this method had been determined by experiment. Hence allowance could be made in each experiment for the loss of naphthalene due to the evaporation of ether. The beaker and the total product recovered were weighed. A measured quantity of standard alkali was then added, followed by water sufficient to cover the solid matter in the beaker. The beaker was next immersed in a steam bath until the naphthalene was melted and the acid products were dissolved. When this had taken place, the mixture was vigorously agitated from time to time and allowed to digest for several minutes. The residual alkali was then titrated with standard acid, using a solution of thymolsulfophthalein as an outside indicator.[13]

OBSERVATIONS MADE AND CALCULATED VALUES RECORDED—The following explanations are offered in connection with the results obtained (Tables II–V):

The "volume of air per 1 g. naphthalene" is the ratio between the total volume of air used (in liters), as shown by the gas meter, and the total naphthalene used, as shown by the loss in weight of the U-tube.

The "time of contact" is the theoretical average time during which a gas molecule may come in contact with the catalyst bed; that is, the time required for the column of gas over the catalyst to move the length of the catalyst bed. It is calculated by the following formula:

$$\frac{\text{Vol. gas over catalyst bed}}{\text{Vol. mixed gases added per sec.} \times \dfrac{\text{temp. in tube} + 273}{\text{temp. in room} + 273}} = \text{Time of contact in seconds}$$

The volume of mixed gases includes the air (measured at room temperature) and the calculated volume of naphthalene vapor at 25°. No account is taken of the penetration of the catalyst bed by the gases.

The "specific time of contact" is the time of contact divided by the volume of gas over 1 sq. cm. of catalyst surface, that is, the time in seconds required for supplying 1 cc. of mixed gases for each sq. cm. of catalyst surface. The purpose of calculating this value is to make the results obtained in tubes of different caliber comparable. The following is the formula used:

$$\frac{\text{Area of catalyst bed}}{\text{Vol. mixed gases added per sec.} \times \dfrac{\text{temp. in tube} + 273}{\text{temp. in room} + 273}} = \text{Specific time of contact}$$

The "temperature" is an average of the pyrometer readings taken at intervals of 10 or 15 min. It represents the average temperature of the gases immediately after leaving the catalyst—*i. e.*, at point P in the figure. The wide variation in temperature shown in Table I is due mainly to a change of view as to the proper temperature to be maintained. In making the first tests it was thought that the temperature should be held as high as possible without ignition of the gases, since the acidity of the products seemed to rise with rise of temperature. Later it was found that temperatures of 450° or higher were unnecessary and undesirable, and the working temperature was reduced to around 425°, and later to around 400°.

The "naphthalene converted" is the naphthalene equivalent to the phthalic anhydride found, expressed as percentage of the total naphthalene added.

The "naphthalene recoverable" is the difference between the acid found and the total product recovered, to which is added the calculated naphthalene lost in evaporation of the ether and the calculated naphthalene carried through the apparatus with the waste gases. The naphthalene lost during the evaporation of 100 cc. of ether as carried out in the analytical work was determined by experiment to be approximately 0.05 g. Since the amount of ether used was ordinarily around 50 cc., the correction generally amounted to 0.02 or 0.03 g. The naphthalene lost with the waste gases was calculated from the vapor pressure of naphthalene, which is given in the literature as 0.064 mm. at 20°, 0.164 mm. at 30°, and 0.378 mm. at 40°.

It was calculated that at 25°, 0.0007 g. of naphthalene would be carried away with each liter of waste gases. The "naphthalene recoverable" is expressed as percentage of the total naphthalene added.

The "naphthalene lost" is the naphthalene not converted and not recoverable, expressed as percentage of the total naphthalene added.

The "acid in product" is the acid found, calculated as phthalic anhydride and expressed as percentage of the total product recovered.

The "yield of anhydride on naphthalene destroyed" is the acid found, calculated as anhydride, and expressed as percentage of the sum of the naphthalene converted and naphthalene lost.

RESULTS OF SEARCH FOR THE BEST CATALYST. DISCUSSION OF TABLE I—The results of the first tests of various substances as catalysts are given in Table I.

Of the 18 substances tested, the oxides of vanadium, molybdenum, tungsten, uranium, manganese, and copper produced more highly acid products than did the other substances, while the oxides of vanadium, columbium, molybdenum, tungsten, uranium, and manganese gave the highest yields. The results show no definite relations between the position of an element in the periodic system and the behavior of the oxide as a catalyst in the reaction under discussion. It is worthy of note, however, that the six substances giving the highest yields were oxides of metals of the fifth, sixth, and seventh groups.

Under the conditions of the experiments, molybdenum trioxide obviously was the best catalyst. It was decided, however, to make further tests of five of the six oxides giving the highest yields. Columbium oxide was eliminated because it was thought to be too rare to be used in a commercial

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[13] This indicator was preferred because the color change taking place is very marked and is not obscured by the dark brown color present in the solution titrated. Furthermore, it is water-soluble, which makes it convenient for use on a spot plate. For description of this compound and its uses, see *J. Am. Chem. Soc.*, **15** (1918), 1443. Phenolphthalein can be used for the titration, but with less convenience and accuracy.

TABLE II—BEST RESULTS OBTAINED IN EXPERIMENTS IN WHICH VARIOUS GAS MIXTURES, TIMES OF CONTACT, AND TEMPERATURES WERE TRIED FOR EACH OF THE CATALYSTS TESTED

Expt. No.	Catalyst	Naphthalene Converted Per cent	Naphthalene Recoverable Per cent	Naphthalene Lost Per cent	Anhydride Produced per Hour Gram	Acid in Product as Anhydride Per cent	Yield of Anhydride on Naphthalene Attacked Per cent
10	V_2O_5	54.8	19.0	26.2	0.99	80.6	78.5
270	MoO_3	18.8	62.6	18.6	0.66	26.2	57.9
279	Wo_3	10.5	39.9	49.6	0.22	24.3	20.1

process. In the additional tests it was planned to vary the ratio of air to naphthalene vapor, the time of contact, and the temperature of the reaction chamber in different experiments with the same catalyst in order to determine whether by changing the conditions of the tests results superior to those of the first series could be obtained. These experiments gave some information on the proper conditions for carrying out this oxidation of naphthalene, and led to a more systematic study of these conditions aiming toward the discovery of the best gas mixture, the best time of contact, and the best temperature. The results of this study will be reported in a subsequent paper.

TABLE III—TESTS OF THE CATALYTIC PROPERTIES OF VANADIUM PENTOXIDE IN DIFFERENT PHYSICAL CONDITIONS

Expt. No.	Description of Experiments[1]	Naphthalene Converted Per cent	Naphthalene Recoverable Per cent	Naphthalene Lost Per cent	Anhydride Produced per Hr. Grams	Acid in Product as Anhydride Per cent	Yield of Anhydride on Naphthalene Attacked Per cent
327	Catalyst; light, fluffy V_2O_5 made from ammonium metavanadate by heating; not heated above 450°	50.6	14.9	34.5	0.98	84.0	68.8
328	Same catalyst used as in Expt. 327 but after heating to 560° and slightly sintering	55.6	21.7	22.7	1.15	76.0	81.8
331	Catalyst; V_2O_5 made from same sample of ammonium metavanadate as catalyst used in Expt. 327 but completely fused and afterwards powdered	61.2	11.7	27.1	1.46	88.0	80.1
334	Catalyst; light V_2O_5 powder—method of preparation unknown	47.4	13.0	39.6	0.84	83.2	63.0
336	Same catalyst used as in Expt. 334 but after heating until slightly sintered	55.1	26.7	18.2	1.13	72.3	87.2
345	Catalyst; V_2O_5 of unknown origin, fused, and then powdered	61.9	14.5	23.6	1.24	86.9	83.5

[1] The conditions with respect to gas mixture, time of contact, and temperature were approximately uniform for the group of experiments.

DISCUSSION OF TABLE II—In tests of uranium trioxide and manganese sesquioxide under varied conditions no yields better than those resulting from the first tests (Table I) were obtained. This was not the case, however, in tests of the oxides of vanadium, molybdenum, and tungsten, of which some results are given in Table II. With these oxides as catalysts it was found that by varying the conditions of the tests, yields much better than those obtained in the first series of experiments could be obtained. For instance, with the same vanadium pentoxide as that used in Expt. 197 (Table I) a yield of 78.5 per cent was obtained, given suitable conditions of gas mixture, time of contact, and temperature. No combination of conditions which would give yields equal to this when molybdenum trioxide was used as a catalyst could be found, notwithstanding the fact that under some conditions (Expt. 271, Table I) this catalyst gave better yields than vanadium pentoxide. Tungsten trioxide was found to be a very poor catalyst in comparison with the oxides of vanadium and molybdenum.

The best yields obtained with each of the three oxides under discussion are shown in Table II. In each test the sample of oxide used was the same as that used to obtain the results reported in Table I.

Molybdenum trioxide not only failed to give yields as high as the best obtained with vanadium pentoxide, but also showed the rather serious fault, from a practical point of view, of being slightly volatile at the reaction temperature. The conclusion was drawn that vanadium pentoxide was the best catalyst, and subsequently in the development of a commercial method for the manufacture of phthalic anhydride this catalyst was used exclusively.

SOME PROPERTIES OF VANADIUM PENTOXIDE AS A CATALYST

FORMS OF VANADIUM PENTOXIDE—When prepared from ammonium metavanadate at temperatures below 300°, vanadium pentoxide is a light, fluffy, chocolate-colored powder. When heated to about 550° it grows somewhat darker and apparently sinters enough to become less fine and fluffy. At a higher temperature (given in the literature as 658°) it fuses, and when cooled again solidifies to a crystalline mass.

In a series of experiments in which at first light, fluffy vanadium pentoxide was used as a catalyst, this oxide was overheated. Apparently it gave better results than when used in the light state. It was found that the oxide had been sintered by the overheating. Further experiments showed that in its catalytic properties light vanadium pentoxide differs somewhat from the sintered or fused forms. It is not known whether this change in catalytic properties is due to physical changes alone or whether chemical changes also occur. It is quite possible that deleterious substances might be volatilized by heating, but this point was not investigated.

DISCUSSION OF TABLE III—The results of a few experiments recorded in Table III furnish some basis for a comparison of the catalytic properties of the oxide in the three forms. With respect to gas mixture, time of contact, and temperature, the conditions were approximately uniform for the whole group of experiments.

It will be noticed that the light oxide and the fused oxide attacked a greater proportion of the naphthalene added and gave a more highly acid product than did the sintered oxide. But the oxide after sintering or fusion gave higher yields than did the oxide in the light state. It must be concluded that it generally is advisable to sinter or fuse vanadium pentoxide for use as a catalyst.

EFFECT OF CERTAIN FOREIGN SUBSTANCES ON CATALYTIC PROPERTIES OF VANADIUM PENTOXIDE

As will be shown in a later article, a great many substances, when present in the reaction chamber with the catalyst during the oxidation of naphthalene to phthalic anhydride, reduce the yield of the anhydride. Substances in the reaction chamber in chemical combination with the catalyst might be expected also to have a deleterious effect. This proved to be true in the case of two substances tested, cobalt metavanadate and vanadium pentoxide containing sodium compounds.

DISCUSSION OF TABLE IV—The results of the test of the two substances mentioned are given in Table IV. The same table shows the results of tests on the effect of sulfur dioxide and of arsenic trioxide on the catalyst. The effect of sulfur dioxide was studied because it was thought that the small amounts of this compound present in the air in industrial centers might poison any vanadium pentoxide catalyst used

TABLE IV—TESTS OF THE EFFECT OF FOREIGN SUBSTANCES ON CATALYTIC PROPERTIES OF VANADIUM PENTOXIDE

Expt. No.	Description of Experiment[1]	Naphthalene			Anhydride Produced per Hr.	Acid in Product as Anhydride	Yield of Anhydride on Naphthalene Attacked
		Converted Per cent	Recoverable Per cent	Lost Per cent	Grams	Per cent	Per cent
335	Test of cobalt metavanadate as a catalyst	19.4	18.5	62.1	0.53	56.5	27.8
340	Test of a sample of V_2O_5 which was found to contain about 4 per cent of sodium	15.3	47.7	36.9	0.23	27.7	33.1
345	Control experiment, V_2O_5 catalyst	61.9	14.5	23.6	1.24	86.9	83.5
346	Test of effect of SO_2. Same catalyst used as in Expt. 345. Enough SO_2 was added to the air used to smell strongly in the effluent gases[2]	61.6	20.4	18.0	1.57	80.3	89.3
347	Test of effect of SO_2. Same catalyst used as in Expts. 345 and 346. Before the experiment, the catalyst was exposed at a temperature of 400° to an atmosphere of undiluted SO_2 for about 1 hour. No SO_2 was added during the experiment	60.4	13.2	26.4	1.48	86.8	80.4
348	Test of effect of SO_2. Same catalyst used as in Expts. 345–347; treated as in Expt. 347 except that treatment was continued for 3 hrs. No SO_2 was added during the experiment	60.9	12.9	26.2	1.42	87.1	80.7
349	Test of effect of As_2O_3. Same sample of V_2O_5 used as catalyst as in Expt. 345, but mixed with 0.1 per cent of its weight of As_2O_3	65.2	11.2	23.6	1.21	90.4	84.9
350	Test of effect of As_2O_3. Same catalyst used as in Expt. 349 but mixed with an additional 0.2 per cent of its weight of As_2O_3[3]	63.0	14.3	22.7	1.16	86.5	85.2

[1] The conditions with respect to gas mixture, time of contact, and temperature were approximately uniform for the group of experiments.

[2] Some sulfuric acid was formed during the experiment. The quantity was determined and taken into account in calculating the results of the experiment.

[3] Some of the As_2O_3 sublimed out of the catalyst before the test was begun.

for a long period in contact with such contaminated air. The effect of arsenic trioxide was tested because this compound is known to act as a poison in other catalytic reactions.

Neither sulfur dioxide nor arsenic trioxide seems to exert any unfavorable influence upon the catalyst and apparently neither substance interferes with the normal course of the reaction. On the contrary, sulfur dioxide actually seems to aid the catalyst, judging from the results of the one experiment (Expt. 346) in which the gas was introduced during the progress of the reaction.

PRODUCTS OF CATALYTIC OXIDATION OF NAPHTHALENE

It has been shown (Expts. 331 and 345, Table III) that naphthalene may be oxidized in the presence of a catalyst under such conditions that the principal solid product obtained will be phthalic anhydride. Some naphthalene generally passes through the reaction chamber unchanged and in addition there are always some brown material and some substance or substances giving the condensate a very sharp, irritating odor. Both the brown coloring matter and the irritating substance are produced most abundantly under certain working conditions which do not yield large proportions of the anhydride.

The by-products of the reaction under discussion have not been carefully studied because, in the laboratory, they are formed only in minute quantities. Some information concerning them has been gathered, however, and methods for their separation from the anhydride have been developed.

The presence of benzoic acid was indicated in all condensates examined by a positive reaction to Mohler's[14] test and by the presence of acid which could be extracted by chloroform from aqueous solutions. In the product resulting from experiments with factory-scale apparatus this acid was found in proportions amounting to about 1 per cent of the total product.

Positive reactions for α- and β-naphthols have been obtained when large quantities of crude condensate made on a factory scale were available for testing. These compounds seem to be present in very small proportions of the whole.

The irritating substance is not much in evidence when the reaction is proceeding smoothly. It is volatile enough to be driven off almost completely when the condensate is dissolved in ether and the ether evaporated, as in the collection of the condensate for analysis. Its vapor, in very moderate concentrations, causes an abundant flow of tears.

The brown coloring matter is soluble in alkaline solution and in the common organic solvents. In chloroform solution it has a bright cherry-red color. It is less volatile than phthalic anhydride.

Both the irritating fumes and the brown coloring matter suggest naphthoquinones, and it seems reasonable to suppose that these compounds, as well as phthalaldehydes, would be formed in the reaction.

Carbon dioxide is the main gaseous product of the reaction, but it is not found in quantities sufficient to account for the total naphthalene destroyed. Carbon monoxide is not found in the gases given off. The conclusion must be drawn that a portion of the naphthalene attacked is broken down into gaseous compounds other than carbon dioxide and carbon monoxide.

SEPARATION OF PHTHALIC ANHYDRIDE FROM BY-PRODUCTS

Fortunately phthalic anhydride can be separated with ease from all of the other substances formed in the catalytic oxidation of naphthalene. One means for accomplishing this separation is fractional sublimation. In the process of sublimation, water, whether free or combined, and naphthalene pass over at lower temperatures than the anhydride does and may be separated quite sharply from it. The anhydride, in turn, may be sublimed away from the colored material, and with proper regulation of conditions may be condensed in a high state of purity, while the colored material is retained in the retort.

The anhydride can also be separated from the crude condensate by crystallization from organic solvents, the color being removed from the solution by means of an adsorbent. For instance, the crude product may be dissolved in warm carbon tetrachloride and a decolorizing charcoal added to remove the color. If the charcoal is then filtered out and the solution cooled in successive stages, successive crops of phthalic anhydride crystals may be recovered while naphthalene is left in the solution.

SUMMARY

1—Naphthalene is oxidized to phthalic anhydride when a mixture of naphthalene vapor and air is passed through a heated tube in the presence of certain catalysts.

2—Vanadium pentoxide is an excellent catalyst for bringing about this reaction; MoO_3 is a fairly good catalyst; while MgO, Al_2O_3, SiO_2, TiO_2, ZrO_2, CeO_2, Cb_2O_5, Cr_2O_3, WO_3, UO_3, Mn_2O_3, Fe_2O_3, NiO, Co_2O_3, Cu_2O, and finely divided Pt mixed with MgO are poor or worthless catalysts.

3—Vanadium pentoxide, fused and then finely powdered, is a better catalyst for this reaction than is the light powder prepared by decomposing ammonium metavanadate at low temperatures.

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[14] *Bull. soc. chim.*, [3] **3** (1890), 414.

4—The value of vanadium pentoxide as a catalyst in the reaction under discussion is not sensibly lowered by arsenic trioxide or sulfur dioxide. The presence of sodium compounds in vanadium pentoxide lowers its efficiency as a catalyst for this reaction.

5—When naphthalene is oxidized under favorable conditions with vanadium pentoxide as a catalyst, phthalic anhydride is the main solid reaction product. Other unidentified solid substances are produced in small quantity. Benzoic acid has been found in the product and naphthols probably are present as a very small proportion of the whole. Carbon dioxide is the main gaseous product, although other unidentified compounds are formed. Carbon monoxide is not found in the gaseous products.

The Nature of Acid Water from Coal Mines and the Determination of Acidity[1,2]

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In connection with an investigation of the corrosive action of acid mine water from coal mines on various types of iron and steel, conducted by the Bureau of Mines for the American Society for Testing Materials, the chemical laboratory of the Bureau determined over an extended period of time the degree of acidity of mine water from a bituminous coal mine in western Pennsylvania. Satisfactory results were not obtained in determining acidity due to free mineral acids by the usual titration method,[3] on account of the presence of a large amount of iron and aluminium sulfates. A general study was accordingly made of the nature of acid mine water from coal mines and of the bearing of sulfates of iron and aluminium on acidity determinations.

Nature or Composition of Mine Water

SOURCE OF SULFURIC ACID—Water from coal mines is usually decidedly acid, containing free sulfuric acid and ferrous, ferric and aluminium sulfates, in addition to sulfates of calcium, magnesium, sodium, and potassium, together with silica and usually some chlorides.

The occurrence of iron sulfates and free sulfuric acid is due to the action of water and air on the pyrite or marcasite associated with coal. These substances are oxidized to ferrous sulfate, ferric sulfate, and sulfuric acid:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

$$4FeSO_4 + 2HS_2O_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$$

NATURAL PRECIPITATE—When acid mine water stands a short time a considerable precipitation of iron-bearing compounds usually occurs. Campbell[4] gives the following typical composition of the natural precipitate, commonly called "sulfur mud:"

	Dry Per cent	Wet Per cent
Moisture	.....	70.50
Silica (SiO_2)	0.70	
Alumina (Al_2O_3)	3.97	
Lime (CaO)	Nil	
Magnesia (MgO)	Nil	
Alkalies ($Na_2O + K_2O$)	Not determined	
Iron oxide (Fe_2O_3)	63.43	
Loss on ignition	31.82	
Sulfur trioxide (SO_3)	14.44	

The composition and character of the colloidal precipitates resulting from the hydrolysis of iron salts have been given considerable study by different investigators.[5] As no definite basic ferric salt has been established with certainty, it is probable that the yellow-brown precipitate consists of hydrous ferric oxides. The presence of sulfur in the natural precipitate is probably due to adsorption of sulfate ions by the colloidal hydrous oxides.

IRON COMPOUNDS—The iron may be considered to exist as soluble ferrous and ferric sulfates together with hydrous ferric oxides in suspension and colloidal solution. On standing, dilution, aeration or warming, insoluble iron compounds tend to precipitate, principally as hydrous ferric oxides.

TYPICAL ACID WATER FROM A BITUMINOUS COAL MINE OF WESTERN PENNSYLVANIA. *Collection of samples*—Samples of water were collected from a bituminous coal mine in the vicinity of Calumet, Pa., the water from which was considered typical of the acid mine water region. The water was collected above ground after it had been pumped from the mine, and contained considerable entrapped air. Before the stoppers were inserted the filled sample bottles were allowed to stand a few minutes to permit the air bubbles to escape. Samples were taken at regular intervals over a period of 6 mo.

Acidity determinations—The unfiltered water was titrated with 0.02 *N* sodium carbonate on the day following collection. The raw water was diluted 1 to 10 before titrating on account of the high concentration of sulfates of iron, which by partial precipitation obscured the end-point when the undiluted water was used. The results obtained by titrating for free mineral acids with methyl orange were unquestionably high, as the result of partial hydrolysis and liberation of free sulfuric acid by aluminium and ferric sulfates. This was confirmed by experimental work in which the ferric sulfate was reduced to ferrous sulfate, before titration, thus eliminating the readily hydrolyzed ferric sulfate. Acidity due to free mineral acids plus sulfates of iron and aluminium was determined by titrating the diluted water at a boiling temperature with 0.02 *N* sodium carbonate in the presence of phenolphthalein. The maximum, minimum, and average acidity of the water during the 6-mo. period are given in Table I.

Table I—Acidity of Typical Water from Bituminous Coal Mine of Western Pennsylvania

Acidity (p. p. m.) in terms of H_2SO_4

No. of Samples Collected	Acidity Due to Free Sulfuric Acid[1]			Acidity Due to Free Sulfuric Acid Plus Sulfates of Iron and Aluminium		
	Max.	Min.	Av.	Max.	Min.	Av.
19	825	590	695	2070	1495	1690

[1] Acidity due to free sulfuric acid is unquestionably too high, as the result of hydrolysis of ferric and aluminium sulfates.

Ferrous and ferric iron—The amount of ferrous and ferric iron present in the unfiltered raw water was determined at different times. The ferrous iron determination was made at the mine on the fresh water, and the total iron determination was made in the laboratory on the day following collection.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] "Standard Methods for the Examination of Water and Sewage," American Public Health Association, **1920**, 41.

[4] Discussion, "Sulfur in Coal and Coke," *Proc. Eng. Soc. Western Penn.*, **36** (1920), 629.

[5] F. K. Cameron and W. O. Robinson, "Ferric Sulfates," *J. Phys. Chem.*, **11** (1907), 641; Eugen Posnjak and H. E. Merwin, "The Hydrated Ferric Oxides," *Am. J. Sci.*, **47** (1919), 339; Harry B. Weiser, "Hydrous Oxides," *J. Phys. Chem.*, **24** (1920), 277.

Ferrous iron was determined on 50-cc. portions of the unfiltered water by adding 40 cc. of sulfuric acid (1:3) and titrating at once to a faint pink with 0.1 *N* potassium permanganate. Ferric iron was calculated from the difference between the total iron and the ferrous iron in the water. The total iron was determined by treating 50-cc. portions of the unfiltered water in a 300-cc. Erlenmeyer flask with 40 cc. of sulfuric acid (1:3) and 5 g. of granulated zinc. The flask was covered with an inverted porcelain crucible lid, and warmed. When the zinc was practically all dissolved the contents of the flask were quickly cooled and filtered through glass wool, washed with distilled water, made up to about 200 cc. with cold distilled water, and titrated at once with 0.1 *N* permanganate. A blank was run with the same amounts of zinc and sulfuric acid. The ferrous and ferric iron content of the water is given in Table II.

TABLE II—FERROUS AND FERRIC IRON CONTENT OF UNFILTERED WATER

Date of Collection	Ferrous Iron P. p. m.	Ferric Iron P. p. m.
October 1, 1920	122	237
October 15, 1920	91	251
October 29, 1920	116	243
November 12, 1920	105	294

As ferrous sulfate oxidizes very readily to ferric sulfate, a number of determinations were made for ferrous iron at the mine and also on the same water the day following collection. In all cases an appreciable oxidation of ferrous iron occurred, although the bottles wêre completely filled with water and tightly stoppered. This oxidation may be accounted for by the presence of dissolved oxygen in the water.

TABLE III—FERROUS IRON CONTENT OF MINE WATER AT MINE AND AFTER STANDING

Date of Collection	At Mine P. p. m.	After Approximately 24 Hrs. P. p m.	Decrease of Ferrous Iron after 24 Hrs. P. p. m.
October 1, 1920	122	94	28
October 6, 1920	91	66	25
October 29, 1920	116	55	61
November 12, 1920	105	89	16

Mineral analysis of water—The mine water as collected was yellow-brown in color and contained some suspended matter. After a short time a considerable precipitation of iron oxides took place. One of the samples was analyzed for mineral content the day following collection and was thoroughly shaken before removing portions for analysis so as to include all mineral matter in solution and suspension. Another sample was allowed to stand in a tightly stoppered glass bottle for about 1 mo., and filtered, and a mineral analysis made on the filtrate. The precipitated matter from this sample amounted to 761 p. p. m. when dried at 105° C. The analytical results on these two samples are given in Table IV.

TABLE IV—MINERAL ANALYSIS OF MINE WATER

CONSTITUENT	Unfiltered Water Analyzed Day Following Collection P. p. m.	Filtrate from Water Allowed to Stand 1 Mo. P. p. m.
SiO_2	60	56
Fe^{++}	101	3
Fe^{+++}	283	263
Al	101	91
Ca	221	224
Mg	87	93
K	5	5
Na	49	53
Cl	9	6
SO_4	2282	2246

The results show that the ferrous sulfate was practically completely removed on standing. After standing, the water contained considerable ferric sulfate in solution, and without doubt an acid concentration had been reached which prevented any further hydrolysis of ferric sulfate and precipitation of hydrous ferric oxides.

DETERMINATION OF ACIDITY

SPECIAL METHODS FOR ESTIMATION OF FREE ACID—The amount of free sulfuric acid in mine water is frequently calculated by making a complete mineral analysis of the filtered water and combining the bases as normal sulfates, the excess SO_4 being figured to free H_2SO_4. This involves much work and is not satisfactory because the value obtained is subject to an error equal to the algebraic sum of the individual errors of the mineral analyses.

Ferric and aluminium sulfates hydrolyze very readily, and waters containing appreciable amounts of these salts invariably give high results when an attempt is made to determine free mineral acids by direct titration with standard alkali and methyl orange.

Capps and Boies[6] removed ferric sulfate by reducing it to ferrous sulfate by means of cadmium amalgam, the air dissolved in the water also being replaced by hydrogen.

Rankin[7] recommends a very simple method of reducing the ferric sulfate to ferrous sulfate by adding an excess of potassium iodide solution to the water and subsequently converting the liberated iodine to sodium iodide by the addition of a slight excess of sodium thiosulfate, measured by the disappearance of the yellow color due to free iodine. The reactions are as follows:

$$Fe_2(SO_4)_3 + 2KI = K_2SO_4 + 2FeSO_4 + 2I$$
$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

The method requires no special apparatus and is extremely simple. It was subjected to experimental tests as to its suitability for the determination of free acid in mine water from coal mines.

DETERMINATION OF FREE ACIDITY—Five samples of water from the Calumet mine were collected at different times, and the acidity due to free mineral acids was determined with and without reducing the ferric sulfate to ferrous sulfate. In the first case, the unfiltered water was diluted and titrated against 0.1 *N* sodium hydroxide, with methyl orange as an indicator. In the reduction method an excess of 10 per cent potassium iodide solution was added to the unfiltered, undiluted water until a yellow color of free iodine appeared; the water was then diluted and titrated. Before the titration the excess of free iodine was destroyed by adding 10 per cent sodium thiosulfate solution. The results of this series of tests are given in Table V.

TABLE V—TITRATION OF FREE MINERAL ACIDS WITH AND WITHOUT REDUCTION OF FERRIC SULFATE

	Acidty (p. p. m.) in terms of H_2SO_4	
Sample No.	Ferric Sulfate not Reduced	Reduced to Ferrous Sulfate
1	665	324
2	688	320
3	865	458
4	715	372
5	670	487

A marked decrease in free acidity after reducing the ferric sulfate is noted in each sample. However, the value obtained must still be considered too high, owing to the presence of aluminium sulfate.

Five synthetic waters with varying amounts of free sulfuric acid were prepared. Ferrous and ferric sulfates and aluminium sulfate were added in approximately the amounts which were found in the acid Calumet mine waters:

	P. p. m.
$FeSO_4$	275
$Fe_2(SO_4)_3$	1000
$Al_2(SO_4)_3$	640

The acid water was titrated before the addition of the salts in order to determine the exact acidity due to added sulfuric acid. Portions of the water were then diluted and titrated for free acidity with and without previous reduction of ferric to ferrous sulfate. The results of the determinations are given in Table VI.

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[6] *J. Phys. Chem.*, **19** (1915), 65.

[7] "Acidity Determination in Water, Leach Liquors, Mine Waters, Etc.," *Chem. Met. Eng.*, **18** (1918), 96.

TABLE VI—TITRATION OF FREE SULFURIC ACID IN SYNTHETIC MINE WATERS
Acidity (p. p. m.) in terms of H_2SO_4

Sample No.	Acidity Due to Added H_2SO_4	Acidity by Titration $Fe_2(SO_4)_3$ Not Reduced	Acidity by Titration $Fe_2(SO_4)_3$ Reduced
1	None	461	294
2	460	1,003	772
3	909	1,403	1,237
4	4,724	4,954	4,782
5	10,025	10,368	10,045

The excess of acidity shown in the unreduced samples apparently consists of free sulfuric acid liberated by the unreduced ferric sulfate. Sample 1, which contained no added acid, showed 294 p. p. m. free acid after the reduction of the ferric sulfate. Doubtless this can be accounted for by the hydrolysis of the aluminium and ferric sulfates during the short interval between the preparation of the water and the reduction of the dissolved ferric sulfate. The excess of free acid determined by titration, after reduction of the ferric sulfate, over that actually added is fairly uniform in Samples 1, 2, and 3, ranging from 294 to 328 p. p. m. Samples 4 and 5, which contained a very large excess of added sulfuric acid, gave by titration after reduction of the ferric sulfate only slightly more free acid than was added. In these waters the very high concentration of free acid apparently prevented hydrolysis of the iron and aluminium sulfates during the interval of time between the preparation of the water and the titration for acidity, and the excess acid shown is probably largely due to hydrolysis of aluminium sulfate during titration. The acid concentration of Samples 4 and 5 is considerably higher than that of acid mine water from bituminous coal mines.

To determine the excess acidity due to hydrolysis of aluminium sulfate, a sample of the Calumet mine water was analyzed for ferrous, ferric, and aluminium sulfates. The first two were determined by titration with standard permanganate as previously described, and aluminium sulfate was determined by a mineral analysis of the water. The calculated acidity due to the sulfates of iron and aluminium was subtracted from the total acidity due to sulfates of iron and aluminium plus free sulfuric acid as determined by titration in the presence of phenolphthalein as an indicator. The difference was considered to represent the true free acidity of the water, due to free sulfuric acid.

Titrations for free acidity due to free sulfuric acid were made on the clear filtered water with and without previous reduction of the ferric sulfate to ferrous sulfate. The results are given in Table VII.

TABLE VII

	P. p. m.	Calculated Acidity in Terms of H_2SO_4 P. p. m.
Sulfates of iron and aluminium, determined by analysis:		
$FeSO_4$	9	6
$Fe_2(SO_4)_3$	966	711
$Al_2(SO_4)_3$	575	494
Calculated acidity due to sulfates of iron and aluminium	...	1211
Total acidity, sulfates of iron and aluminium plus free sulfuric acid	...	1510
Difference acidity due to free sulfuric acid	...	299
Titrated free acidity after reduction of ferric sulfate	...	372
Titrated free acidity without reduction of ferric sulfate	...	715

The mine water had stood for some time in the laboratory after collection and considerable deposition of iron compounds had occurred. The ferrous iron had been practically entirely oxidized to ferric iron.

If 299 p. p. m. be taken as the true acidity due to free sulfuric acid, the titration method with previous reduction of the ferric sulfate gave results only 73 p. p. m. too high, while the titration without previous reduction of the ferric sulfate gave results 416 p. p. m. too high. This indicates clearly that fairly satisfactory results for free acidity can be obtained if the ferric sulfate is reduced previous to titration. If extreme accuracy is desired, a correction can be made for the water in question by calculating the effect of the aluminium sulfate present and deducting this from the value for free acidity determined by reduction of the ferric sulfate and subsequent titration. With waters of unknown aluminium sulfate content, the degree of free acidity can best be calculated from the total acidity determined by titration in the presence of phenolphthalein, and the acidity due to sulfates of iron and aluminium, as calculated from the analysis of the water. In a series of acidity determinations on the same water, if the aluminium sulfate content does not vary greatly from time to time, a correction for the water in question could be calculated and deducted from the titrated free acidity after previous reduction of the ferric sulfate.

As this method of calculation of free sulfuric acid in mine water assumes that the ferrous and ferric iron determined by titration are present as normal sulfates, it is necessary to filter the water to remove any insoluble suspended hydrous ferric oxides.

DETERMINATION OF TOTAL ACIDITY—The total acidity due to free mineral acids plus sulfates of iron and aluminium can be determined satisfactorily by a direct titration at a boiling temperature with standard alkali in the presence of phenolphthalein as an indicator. The indicator shows an acid reaction until the free acid has been neutralized, and sulfates of iron and aluminium have been converted to hydroxides.

Mine water usually contains appreciable amounts of calcium sulfate in solution. A saturated solution of calcium sulfate in water was titrated at a boiling temperature to a faint pink with both NaOH and Na_2CO_3 solutions with phenolphthalein as an indicator; no difference in results was obtained. The amount of sodium hydroxide or carbonate required was the same as with the same quantity of distilled water.

Precipitation of insoluble calcium carbonate will occur if a considerable excess of sodium carbonate is added. This excess, however, is considerably greater than that necessary to give a pink end-point after the neutralization of free acid and sulfates of iron and aluminium.

Probably, for all practical purposes, the determination of total acidity due to free mineral acids plus sulfates of iron and aluminium is of as great importance as the actual free acid present in the mine water. As the free acid is neutralized or the water diluted, the sulfates of iron and aluminium will hydrolyze and liberate more acid. These sulfates may be considered as latent sources of free acid and play a very important role in the corrosive action of mine water.

SUMMARY

Direct titration of acid mine water for free sulfuric acid with alkali solutions in the presence of methyl orange will give too high results, on account of hydrolysis of ferric and aluminium sulfates. Reduction of ferric sulfate previous to titration gives more nearly correct free acid values. A correction for the hydrolysis of the aluminium sulfate can be applied.

ACKNOWLEDGMENTS

The authors are indebted to Mr. A. C. Fieldner, Supervising Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, for many helpful suggestions, and to Mr. J. R. Campbell, Chief Chemist, H. C. Frick Coke Co., for much valuable information on mine water.

A Preliminary Study of the Activated Sludge Process[1]

By John Arthur Wilson, William R. Copeland and Henry Mills Heisig

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In October 1920, an investigation was begun in this laboratory to determine the cause of periodic recurrences of difficulties in filter-pressing sewage sludge from the activated sludge process. Our first experiments showed that the variation in rate of filtration with the hydrogen-ion concentration of the sludge is so great as to make the control of this factor essential to the efficient operation of the plant. In fact it was found that adding sufficient sulfuric acid to the sludge to reduce its pH value from 8 to 3 generally reduced the time required to filter a given quantity by 80 per cent. The increase in efficiency in the big plant is even greater because the rapidly filtering sludge leaves the filter bags in the press clean enough to be used again without washing, which is not the case with untreated sludge. Later it was found that the use of aluminium sulfate and similar salts in conjunction with hydrogen-ion control gave rates of filtration about twice as great as were possible by change of acidity alone. Some of these experiments have already been reported in earlier papers.[2,3]

Careful studies of the effect of hydrogen-ion concentration upon the rate of filtration of sludges obtained throughout the year made it evident that hydrogen-ion control, tremendously important in itself, is not the only factor vital to the efficient operation of the plant. Sludge obtained during February, when the temperature of the raw sewage was 12°, required eighteen times as long to filter as sludge obtained during August, when the temperature had risen to 21°, even though each sample was brought to its optimum acidity before filtering. It became clear that an entirely satisfactory solution of the filter-pressing problem involved a reasonably complete investigation of the entire activated sludge process. A search of the literature revealed that very little has been accomplished towards an explanation of the mechanism of the process, and we have therefore begun an investigation with this object in view. While the work is still incomplete, it has seemed desirable to take advantage of this occasion to present what has been accomplished in the hope of stimulating other activities along these lines.

The most trying period of the year is the first quarter, when the temperature of the raw sewage is lowest. But even during this period it is possible to make the purity of the effluent discharged into the lake meet the requirements set, although the condition of the sludge for dewatering is then very poor.

Method of Defining the Condition of Sludge

An important discovery in this investigation was the fact that the condition of a sludge can be defined satisfactorily by the curve representing its rate of filtration under fixed conditions as a function of the hydrogen-ion concentration. In making this determination in this work, we first dilute the sludge to contain 1 per cent of solid matter. The filtering equipment consists of 20 Büchner funnels set in filter flasks all connected with one pump furnishing a high and practically constant vacuum. Twenty portions of sludge, of 450 cc. each, are treated with 50 cc. of sulfuric acid solutions of different concentrations so as to give a range of pH values from 2 to 8. All samples are thrown on the filters at the same time, the number of minutes required for complete filtration is noted, and the pH values of the filtrates determined. As soon as any sample is completely filtered, its flask is cut off from the main line so as not to reduce the vacuum on the others. The number of minutes required for filtration is plotted against the pH value found. The curve is a measure of the condition of the sludge and indicates not only the efficiency with which it can be filter-pressed, but also the rate at which it is becoming septic. These curves will be referred to hereafter as "condition curves" of the sludge.

Changes in Condition of Sludge during the Year

Fig. 1 shows condition curves of representative samples of sludge taken during each month of the present year to date. In order to handle the sludge of February, more than eighteen times as many filter presses would be required as would be needed to handle the August sludge, even with the most rigid hydrogen-ion control. The lowest temperature of the raw sewage was 7° on March 8, and the highest was 23° on July 21 and 22. Unfortunately the curves cannot be used as a measure of the effect of temperature alone on the condition of the sludge because of changes in the raw sewage brought about by the industrial depression. During the coldest period, the amount of solid matter in the sewage was unusually low, necessitating a longer time for its collection after the aeration. The condition of the sludge becomes worse the longer it is allowed to stand after aeration, apparently because of septic action.

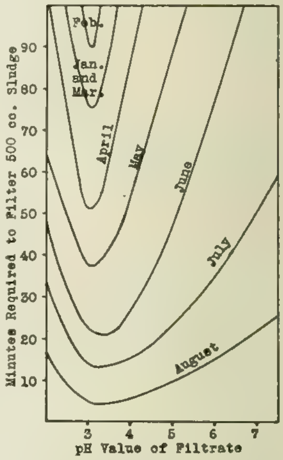

FIG. 1
Showing how the condition of the sludge from the activated sludge process varied from January to August 1921

Aeration *vs.* Septic Action

A sample of July sludge was allowed to stand over night in a warm place. Next day it was quite foul and its condition curve changed from that of July sludge to that of February sludge shown in Fig. 1. Aerating this septic sludge for 2.5 hrs. brought its condition curve almost to that of May sludge, whereas 5 hrs. of aerating brought it almost to that of June sludge. Further experiment showed that the curves in Fig. 1 are all obtainable with any sludge; the lower curves can be raised by allowing the sludge to stand, while the higher curves can be lowered by aerating the sludge sufficiently long, the change apparently being reversible. This fact offers a solution of the filter-pressing problem during cold weather. While the cost of heating 85 million gallons of raw sewage daily during the cold weather would be prohibitive, it is apparently quite feasible to heat the sludge obtained from this amount of sewage and re-aerate it. It is conceivable that this will make for uniform pressing conditions all year round, which would be of enormous value, as the curves in Fig. 1 indicate.

The effect of hydrogen-ion concentration upon the septic action is shown in Fig. 2. A sludge already in very poor condition was used and condition curves were obtained with only 100-cc. portions of the sludge because of its poor condition. A second series was treated with acid, but was kept 24 hrs. before filtering. It will be noted that the septic action proceeds at the greatest rate at a pH value between 5 and 6. This action proceeds slowly at temperatures under 20°, but very rapidly at higher temperatures, and the rate is an accelerated one.

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[1] Presented before the Division of Water, Sewage and Sanitation Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] "Role of Acidity in the Dehydration of Sewage Sludge," THIS JOURNAL, **13** (1921), 406.

[3] "Application of Colloid Chemistry to the Filter Pressing of Sewage Sludge," *J. Am. Water Works Assoc.*, **8** (1921), 486.

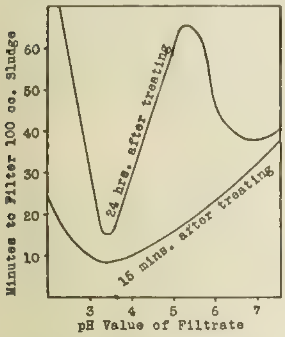

FIG. 2
Showing how septic action is dependent upon hydrogen-ion concentration. A more septic sludge filters more slowly

The effect of hydrogen-ion concentration upon aeration has not yet been intensively studied. A single experiment made upon the re-aeration of sludge showed practically the same result whether the pH value of the sludge was 8 or 3. Further work will soon be under way.

In order to study the effect of temperature upon the re-aeration of sludge, three stoneware cylinders were equipped as aerating tanks. In the bottom of each was placed a Filtros plate having an area of 1 sq. ft. through which air could be forced. Each cylinder had a diameter of 15 in. For each experiment 66 gal. of sludge containing 1 per cent of solid matter were used and air was forced through at the rate of 0.45 cu. ft. per min. Each cylinder was surrounded by a cooling or warming jacket and the temperature was maintained by means of water warmed with steam or cooled with ice.

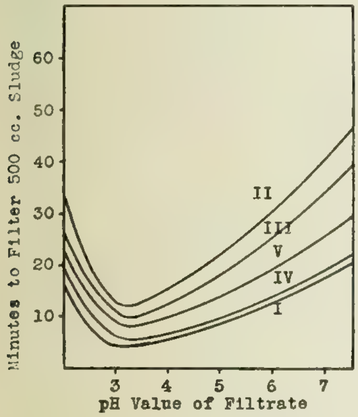

FIG. 3

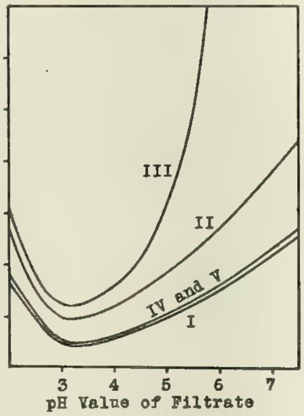

FIG. 4

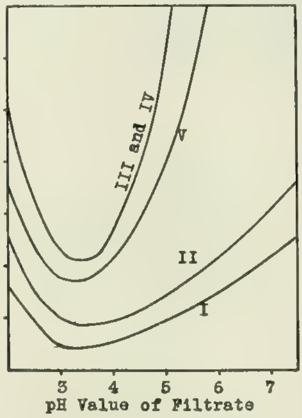

FIG. 5

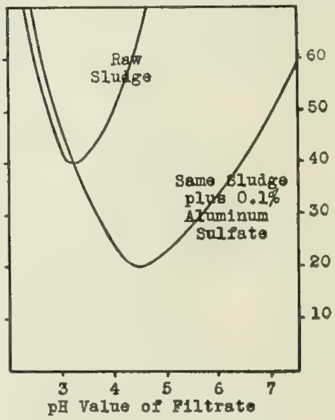

FIG. 6

FIG. 3—Showing the effect of temperature upon the efficiency of re-aerating sludge. I—Fresh sludge. II—Same after standing 45 hrs. III—Same after aerating 5 hrs at 11°. IV—Same as II, but after aerating 5 hrs at 22°. V—Same as II, but after aerating 5 hrs. at 34°

FIG. 4—Showing effect of the nature of the gas upon the efficiency of re-aerating sludge. I—Fresh sludge. II—Same after standing over night. III—Same after aerating 4 hrs. with hydrogen. IV—Same as II after aerating 4 hrs. with oxygen. V—Same as II after aerating 4 hrs. with air

FIG. 5—Same as Fig. 4 except that the sludge was covered with xylene during aeration

FIG. 6—Showing the effect of aluminium sulfate upon the condition of sludge

A set of experiments is shown in Fig. 3. Curve I represents a sample of August sludge in excellent condition; Curve II this same sludge after standing for 45 hrs. at 20°. Portions of the sludge after standing were put into the 3 cylinders. The temperature of the first was maintained at 11°, the second 22°, and the third 34°. Each was aerated for 5 hrs. Apparently there is an optimum temperature of aeration lying between 11° and 34°, since better results were obtained at 22°. The experiment was repeated with the same result. The work will soon be extended to other temperatures and to sludges in a more septic condition. August sludge does not become septic rapidly at 20°.

The same cylinders were used to study the effect of the nature of the gas employed. During ordinary aeration, oxidation and nitrification of the sludge take place but whether these are essential to bring the sludge into good condition for pressing is not yet clear. In Fig. 4, Curve I represents a good August sludge and Curve II shows the same sludge after standing over night. This sludge was then put into the cylinders at a temperature at 20°. The cylinders were covered to prevent the entrance of air as much as possible and the samples were aerated for 4 hrs., the first with hydrogen, the second with oxygen, and the third with air. Hydrogen made the sludge worse, while oxygen and air improved it to an equal degree and brought it back almost to its condition before standing over night.

The above experiment was repeated except for covering each sludge during aeration with a layer of xylene. The presence of the xylene entirely altered the results; all gases now made the condition of the sludge worse. Fig. 5 shows that hydrogen and oxygen now behave exactly alike, while air does not do so much harm.

DISCUSSION

Sufficient data are not yet available to form a sound theory of the mechanism of the activated sludge process, but speculation is desirable at this stage as a guide in outlining further experiments. It is generally conceded that putrefaction is usually due to bacteria or enzymes, both of which are present in the sludge. Whether or not bacteria and enzymes are essential to the aeration process is not so clear. The question may be asked: Is the action aeration *vs.* putrefaction really a conflict between certain aerobic and anaerobic bacteria? The fact that the aeration action is more effective at 22° than at 34° makes it doubtful that ordinary enzymes are responsible, as these operate more effectively as the temperature is raised to 40°. This would also be borne out by the fact that aeration in one test was as effective at a pH value of 3 as at 8. On the other hand, the action is not merely mechanical, since hydrogen makes the sludge worse, whereas oxygen or air makes it better. But the presence of xylene renders the oxygen of no more value than the hydrogen. Is the action of the xylene to retard the action of aerobic bacteria or does it prevent some chemical action by becoming adsorbed by the surface of the sludge? Mechanical action alone, if sufficiently vigorous, will make the condition of the sludge worse. This constitutes a serious difficulty in attempting to use the centrifuge for dewatering sludge.

Whatever may be the initial cause of the aeration action, the ultimate change appears to be chemical. Good flocks were obtained by adding aluminium sulfate or sodium phosphate to the raw sewage, but not by adding sulfuric acid or lime. The cost of such treatment, however, was found to be much greater than aeration, with results not as good. The addition of aluminium sulfate to sludge lowers its condition curve, but at the same time changes its point of optimum hydrogen-ion concentration to a point between the isoelectric point of alumina and that of the sludge before adding aluminium sulfate. This is shown in Fig. 6. Re-aeration of sludge lowers its condition curve, but not its point of optimum hydrogen-ion concentration. All curves in Fig. 1 have points of minimum at about 3.2. Does this suggest that the fundamental action of aeration is different from that of the aluminium sulfate? It is hoped that the line of experimenting recently begun may lead to a practically complete solution of this complex problem, at least so far as the most efficient chemical control of the plant is concerned.

The Chemical Constituents of Skin[1]

By F. L. Seymour-Jones

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It is the object of this paper to present very briefly a survey of the chemical constituents of skin, regarded, as far as may be possible, as chemical individuals. In recent years two general papers on skin chemistry have appeared, one, written about 1910 but published posthumously, by R. A. Seymour-Jones,[1,*] and the other, published in 1920, by G. L. Terrasse.[2] These summarize the work on the subject, but deal more particularly with the structure of the hide proteins and the conception of amino acids as "Bausteine" in protein composition. It is proposed in the present paper to deal with matters unconsidered in the above papers, or from viewpoints which have arisen since their compilation.

Work on the Swelling of Gelatin

The work of Procter[3] and his collaborators on the acid swelling of gelatin has proved of fundamental importance in dealing with proteins in general. This has resulted in the deduction of mathematical formulas by which the distribution of ions in the gelatin (or other protein) and in the external solution can, under given conditions, be calculated. In place of a series of obscure phenomena, necessitating individual measurements for each case, we now have a definite stoichiometrical relationship based on applications of osmotic equilibria and Donnan's theory of membrane equilibria.

This theory of gelatin swelling depends, however, on a definite conception of the molecular structure of gelatin. Procter regards gelatin jellies and solutions as composed of a network of molecular dimensions. This permits the development of osmotic effects, while ions within the jelly remain within the range of molecular attractions. In a protein jelly the term "molecular" may, however, cover a relatively large space. Bütschli has formulated a theory in which the jelly is presumed to have a network of microscopic dimensions, while Quincke considers a jelly to be of two phases, a colloid-poor and a colloid-rich phase, the one dispersed in droplets throughout the other. This last view has met with considerable support, but, on the whole, the evidence favors Procter's view.

Work on Isoelectric Point of Proteins

Arising from the work on gelatin swelling, most important results have been obtained in the researches of Jacques Loeb,[4] who has clearly shown the importance of taking into account the isoelectric point of proteins and the hydrion concentration of solutions employed. The isoelectric point (I. E. P.) has been shown to be, for proteins in general, coincident with the points of minimum swelling, conductivity, osmotic pressure, viscosity, and solubility. For gelatin,[†] determinations vary from pH 4.5–4.7, and the value may be taken as about 4.6. No figures have been published yet for skin proteins in general, but work at Leeds University on hide powder gives the figure 4.8 for collagen.

The importance of this figure lies in the fact that proteins in general are amphoteric. Loeb has shown for gelatin, and the same probably applies to hide proteins in general, that at a pH greater than its isoelectric point it functions only as an acid, and at a less pH only as a base. Thus, when gelatin was treated with silver nitrate and subsequently washed to remove excess of the salt at pH 3.6 to 4.7, no silver combined with the gelatin, whereas above 4.7 silver combined with the gelatin. Below 4.7 gelatin nitrate exists and above 4.7 silver gelatinate.

As a practical example, consider the disinfection of raw hides with formic acid and mercuric chloride. Under the conditions specified by the process, the pH is such that no mercury can combine with the hide substance. Consequently if the hides are washed prior to liming (or other alkaline treatment) all the mercury is removed. If the mercury ion is not so removed, it will be fixed in the limes, and black stains will occur in subsequent processes.

Using equivalent solutions of bases, Loeb found that all monacid bases gave a swelling, viscosity, and osmotic pressure practically identical, but considerably greater than di-acid bases. The same applies to acids; all functioning as monobasic acids gave practically identical curves, while dibasic acids (*e. g.*, sulfuric, and to a lesser extent oxalic) gave curves of diminished swelling, etc. This identity, however, applies only when plotting pH against the property measured; that is, the amount of acid present may vary considerably, but, provided the pH's be identical, all monobasic acids will swell the protein to the same extent.

In this fact lies the explanation of the mystery of the "Hofmeister" or "lyotrope" series, a curious sequence of ions arranged in the order in which they affect the properties of colloids. In the compilation of this series, the factor of hydrion concentration was neglected. Provided all excess of the reacting salt is removed, the various properties of proteins, such as swelling, viscosity, osmotic pressure, etc., are in reality functions of the hydrion concentration.

All this is of great importance in considering the effect of any reagent on the hide proteins. To take a case in point: It will have been noticed that the isoelectric point for gelatin, and presumably for collagen, lies decidedly on the acid side of the point of true neutrality. The actual curve for gelatin, where swelling is plotted against pH, shows a fairly sharp rise to a maximum at about 2.4, a fall to a minimum at 4.6, and a slow gradual rise to a maximum at about 12. If a hide is in a liquor of pH 2, for example,[3] decreasing the acidity will increase the swelling until a pH of 2.4 is reached, then will decrease the swelling to a pH of 4.6. Similarly, for a hide in liquor of pH 6, increasing acidity will decrease the swelling until a pH of 4.6 is reached. And all this is on the acid side of the neutral point. The importance of the swelling curve in relation to pH is then obvious in tan liquors, the manufacture of synthetic tannins, and the like.

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[1] Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[*] Numbers in the text refer to Bibliography.

[†] Michaelis, 4.7; D. Jordan Lloyd, 4.6; Loeb, 4.7; M. H. Fischer, 4.5.

Constituents of Hide

The individual constituents of hide may be divided into proteins, fats, and mineral salts.

The mineral salts consist of phosphates and aluminates in very small quantity associated with keratin in the epidermis and of small quantities of various mineral substances, chiefly sodium and potassium chlorides, calcium and magnesium phosphates, in the blood. In the latter also occurs hematin, a highly complex organic iron salt. Generally speaking, the mineral constituents of skin are negligible.

The proteins are mainly scleroproteins or albuminoids (*i. e.*, miscellaneous proteins not allotted to any group), but also include some albumins and globulins.

COLLAGEN—Of the proteins, the most important to the tanner is collagen, which forms the constituent of the white fibers of the corium. It contains carbon, hydrogen, nitrogen, oxygen, and perhaps a little sulfur. Analyses vary slightly, indicating that conceivably there may be more than one collagen, but the difficulty of obtaining a pure product probably explains the variations.

In fresh hide the white collagenous fibers are somewhat swollen and hydrated. The normal method of purification, which is used in practice, consists in washing, liming, unhairing, deliming, bating, and scudding, thus removing keratins, mucins, and elastins. Such a collagen is hide powder.

As to structure, it has been argued that collagen has a ring formation, since trypsin will not act on it unless it be previously swollen with acid or alkali, or treated with pepsin. On the other hand, many synthetic polypeptides cannot be hydrolyzed by trypsin, but still possess an open chain structure.

From the fact that boiling collagen with water hydrolyzes it to gelatin, and from the general similarity between the two, it is commonly supposed that collagen is an anhydride of gelatin.[5] Furthermore, gelatin heated above 100° is gradually converted into an insoluble substance which, apart from its lack of fibrous structure, closely resembles collagen. Since it is impossible to obtain gelatin again from this by mere boiling,[6] this argument is of doubtful value. It is known that hide dried at 60° for some hours cannot be softened back, and this is similar to the effect of heat on gelatin. Merely as a suggestion, this hardening on heating may be similar in origin to the coagulation of egg albumen. Analysis does not help in determining the question; the similarity in the figures is great. Collagen has a slightly higher carbon content than gelatin, but is lower in nitrogen, the differences being too small for definite conclusions. On the other hand, collagen gives positive Millon and xanthoproteic tests, indicating the presence of tyrosine and phenylalanine, tests which are negative or only very slightly positive with gelatin.

Collagen forms salts, just as gelatin does, and we may have, for instance, collagen chloride and lime collagenate, depending on the pH's of the solutions employed. There can be but little doubt that collagen is appreciably changed during the earlier processes of leather manufacture, and hence the collagen of fresh and delimed hide is not necessarily identical. The slow hydrolysis of collagen, by alkalies or acids, has not been studied.

The formation of salts by collagen is of importance in the theory of tanning. There is now no reason for doubting the formation of collagen tannates, collagen chromates, or chromium collagenates, as the case may be. But this is not to say that one single theory will explain every type of tannage. So many substances can be used to tan leather that no one explanation can at present cover all. Further, Shorter[7] found that the electrical reactions of skin varied according to tannage. With raw hide and wool rubbed together, the hide had a negative and the wool a positive charge; the same applied to oil leather and wool, but with vegetable tanned leather and wool, the wool had a negative and the leather a positive charge.

ELASTIN—The most stable protein of hide is elastin, found in the yellow elastic fibers. It also occurs in many tendons of the body, including the *ligamentum nuchae*, the tendon at the back of the ox's head, and it is the elastin from these sources rather than that of the skin which has been most studied. It has extraordinary elastic properties. The writer found that a piece of *ligamentum nuchae* of about 1 cm. square section gave on a testing machine an extension of 150 per cent before breaking, the strain being too small to measure (*i. e.*, less than 5 lbs.). Elastin is not completely dissolved on boiling with water, is scarcely attacked by acetic acid or cold or hot 1 per cent alkali, and apparently does not combine with tannin or chrome. The writer found that *ligamentum nuchae* is, however, slowly digested by lime solutions, though this may be due to bacteria. It is very slightly attacked by pepsin, but more readily by trypsin, especially if previously boiled, or treated with acids or alcohol. The previous treatment of pelts with alkaline solutions may affect the elastin so as to render it less resistant to trypsin. It can be separated from hide by merely boiling after unhairing, the scutch remaining consisting of elastin, possibly somewhat changed in process.

KERATIN—Keratins occur in the epidermis, hair, hair sheaths, walls of sudoriferous and sebaceous glands, and cell walls in the blood. Usually they are classed as "old" or "young" keratin, the latter forming the basal layers of the epidermis. The chief difference is that young keratin is more easily hydrolyzed than is old keratin by the action of proteoclastic enzymes (*e. g.*, trypsin and pepsin) or dilute alkali. Both are insoluble in water, except on boiling under pressure; they are hydrolyzed by concentrated alkali or sodium sulfide solutions. Since dilute acids may be used to unhair,[8] possibly young keratin is soluble therein.

MUCIN—Mucins occur in the so-called "coriin" or cementing substance. Procter regards this as some substance "nearly identical with, but somewhat more soluble than that of the fibrils themselves."[9] It is easily soluble in dilute acid or alkali. Van Lier[10] found it was rather a mucoid, and was usually contaminated with nucleoproteins. By repeated extraction of pelt with half saturated lime water, he found no more could be obtained and therefore claimed that it is not a hydrolytic decomposition product of collagen. It is precipitated by 5 per cent acetic acid, but is soluble in excess; the precipitate consists of a mass of stringy fibers. It is soluble in 1 to 2 per cent hydrochloric acid, and, on boiling some time, reduces Fehling solution. Ox, horse, and calf mucoid appear identical, but they differ from mucoid obtained from tendons. Eitner[11] states that it is rendered less soluble on drying at a high temperature. Long liming will obviously open up the fibers by dissolving the coriin.

The blood and lymph in skin are responsible for the presence of serum-albumin and globulin, fibrin, and keratins of the cell walls. Albumin combines with tannin, but is usually removed by soaking and liming.

FATS—The fats of the fat cells consist chiefly of lecithins and cholesterols, *i. e.*, mixed triglycerides, in which a complex phosphoric acid-choline radical replaces one hydroxyl, and alcohols. In certain sebaceous glands cetyl and octodecyl alcohols have been reported. Unfortunately our knowledge of the skin fats is still very limited, and other bodies may also be present in the fat cells.

Much yet remains to be done before the chemistry of skin can be considered to be thoroughly understood, but though progress has been slow in the past, each forward step materially widens the path for those who follow. In any case, it is only through a sounder knowledge of the basic raw material that the art and science of leather manufacture can hope to make progress.

BIBLIOGRAPHY

1—"The Chemistry of Skin," *Collegium* (London), **1915**, 288.

2—"Hide Substance," *J. Am. Leather Chem. Assoc.*, **15** (1920), 608.

3—H. R. Procter, "Über die Einwirkung verdünnter Säuren and Salzlosüngen auf Gelatine," *Koll. Chem. Beihefte*, **2** (1911), 203; "Equilibrium of Dilute Hydrochloric Acid and Gelatin," *J. Chem. Soc.*, **105** (1914), 313; "The Combination of Acids and Hide Substance," *Collegium* (London), **1915**, 3; H. R. Procter and D. Burton, "The Swelling of Gelatinous Tissues," *J. Soc. Chem. Ind.*, **35** (1916), 404; H. R. Procter and J. A. Wilson, "The Acid-Gelatin Equilibrium," *J. Chem. Soc.*, **109** (1916), 307; "The Swelling of Colloid Jellies," *J. Am. Leather Chem. Assoc.*, **11** (1916), 399; "Theory of Vegetable Tanning," *J. Chem. Soc.*, **109** (1916), 1328; J. A. Wilson, "Theory of Colloids," *J. Am. Chem. Soc.*, **38** (1916), 1982; H. R. Procter, "The Swelling of Gelatin," *J. Soc. Leather Trades' Chem.*, **2** (1918), 73. See also articles in "Colloid Chemistry Reports," I and III, by H. R. Procter and J. A. Wilson, and bibliographies there given.

4—See Loeb, *J. Gen. Physiol.*, from commencement to present date.

5—Hofmeister, *Dinglers polytech. J.*, **205** (1872), 164.

6—Procter, "Principles of Leather Manufacture," 58.

7—Shorter, *J. Soc. Dyers Colour*, **36** (1920).

8—Thuau, *Collegium*, **1908**, 362; Nihoul, *Bourse aux Cuirs de Liège*, **1908**; Marriott, *J. Soc. Leather Trades' Chem.*, **5** (1921), 2.

9—"Colloid Chemistry Reports," **1917**, 10.

10—*Z. physiol. Chem.*, **61** (1909), 117; *Collegium*, **1909**.

11—*Gerber*, **1880**, 111, *et seq.*

Influence of Sodium Chloride, Sodium Sulfate, and Sucrose on the Combination of Chromic Ion with Hide Substance[1,2]

By **Arthur W. Thomas[3] and Stuart B. Foster**

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Continuation of the authors' work offers evidence that the retarding action of neutral salts in chrome tanning is due to the formation of addition compounds, with hydration as a secondary cause.

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The significance of the presence of neutral salts in chrome liquors was first shown by Wilson and Kern,[4] and several studies of their effects have been published from this laboratory.[5] Recently Wilson and Kern[6] made a further investigation of the question and suggested as an hypothesis that the retarding action on the chrome tanning might be due to hydration by the added salt, resulting in an actual increase in the concentration of chromic ion. Since Miss Baldwin[7] had found that increase in concentration of a chrome liquor over 16 g. Cr_2O_3 per liter resulted in a diminution of the amount of chromium fixed by hide substance, this hypothesis appeared reasonable.

If hydration did take place, the concentration of hydrogen ion should be increased as well as that of the chrome. That this was actually the case with chlorides was shown by Thomas and Baldwin,[8] but at the same time they demonstrated that sulfates lower the hydrogen-ion concentration of acid solutions, as measured by the hydrogen electrode. Since Wilson and Kern found that sodium sulfate decreased the fixation of chrome, just as sodium chloride and other chlorides did, they were obliged to admit another possible factor, namely, the formation of addition compounds between the chromium salt and added sulfate as well as between the acid present and added sulfate.

With the view of approaching a solution of this question the following experiments were carried out. In addition to sodium chloride and sulfate, the former raising the C_{H^+} and the latter lowering it, sucrose was selected as a hydrating nonelectrolyte since H. C. Jones[9] has shown that it hydrates considerably in aqueous solution. Inasmuch as Thomas and Kelly[10] had shown that in a period of 48 hrs.' contact the maximum combination of chrome with hide substance was effected by a chrome liquor containing 15.5 g. Cr_2O_3 per liter, three sets of liquors were selected, one containing 15.5 g. Cr_2O_3 per liter, and two others 3 g. and 100 g. Cr_2O_3 per liter.

MATERIALS AND TECHNIC

1920 and 1921 American Standard Hide Powder served as the source of hide substance. The chrome liquors were prepared by dilution of pure concentrated liquors made by reduction of chemically pure sodium dichromate with sulfurous acid, as described by Thomas and Kelly.[11]

Portions of hide powder equal to 5 g. of absolutely dry substance were covered with 50 cc. of distilled water in bottles, and allowed to stand over night, when the salts or sugar to give the desired concentrations were added. Finally 150 cc. of chrome liquor were added, of such a concentration that if it were diluted to 200 cc., it would contain 3, 15.5 or 100 g. Cr_2O_3 per liter. The mixtures were rotated in a tumbling machine for 48 hrs., filtered through muslin bags, and washed well with tap water and three times with 200-cc. portions of distilled water. The powder was air-dried at 30° C., then at 100° C., and finally allowed to come to equilibrium with atmospheric humidity. Moisture, nitrogen, and chromium were determined. Multiplication of the per cent nitrogen by 5.614 gave per cent hide substance. All figures in the tables are on the moisture-free basis.

TABLE I (LIQUOR CONTAINED 3 G. Cr_2O_3 PER LITER)

Concentration of Salt M	Protein Per cent	Cr_2O_3 Per cent	Mg. Cr_2O_3 per G. Hide Substance
($NaCl$)			
0	83.75	4.44	53
0.5	88.01	3.62	41
1	90.03	3.16	35
2	90.37	3.45	38
3	88.05	3.75	43
4	87.58	4.19	48
(Na_2SO_4)			
0.5	90.71	4.35	48
1	91.27	3.19	35
2	93.12	2.13	23
3	91.82	2.11	23

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[1] Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 381 from the Chemical Laboratories of Columbia University.

[3] Assistant Professor.

[4] *J. Am. Leather Chem. Assoc.*, **12** (1917), 445.

[5] *Ibid.*, **13** (1918), 248; **14** (1919), 10; *J. Am. Chem. Soc.*, **41** (1919), 1981.

[6] *J. Am. Leather Chem. Assoc.*, **15** (1920), 273.

[7] *Ibid.*, **14** (1919), 433.

[8] *J. Am. Chem. Soc.*, **41** (1919), 1981.

[9] *Carnegie Inst. Publ.*, **60** (1907).

[10] THIS JOURNAL, **13** (1921), 31.

[11] *J. Am. Leather Chem. Assoc.*, **15** (1920), 665.

Measurements of the hydrogen-ion concentration of the liquors belonging to Table II verified the contrasting effects of sodium chloride and of sodium sulfate previously reported from this laboratory.

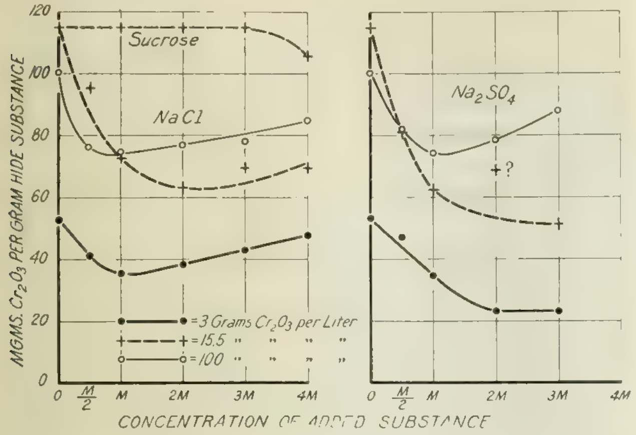

FIG. 1

TABLE II (15.5 G. Cr_2O_3 PER LITER)

Concentration of Salt M	Protein Per cent	Cr_2O_3 Per cent	Mg. Cr_2O_3 per G. Hide Substance
(NaCl)			
0	77.92	9.01	116
0.5	79.18	7.59	96
1	81.27	5.93	73
2	82.86	5.26	63
3	84.38	5.90	70
4	83.93	5.85	70
(Na_2SO_4)			
0.5	81.07	6.58	81
1	84.32	5.29	63
2	83.48	5.76	69
3	85.44	4.36	51

TABLE III (100 G. Cr_2O_3 PER LITER)

Concentration of Salt M	Protein Per cent	Cr_2O_3 Per cent	Mg. Cr_2O_3 per G. Hide Substance
(NaCl)			
0	75.57	7.70	101
0.5	80.78	6.17	76
1	82.13	6.15	75
2	82.42	6.35	77
3	81.23	6.35	79
4	79.10	6.77	86
(Na_2SO_4)			
0.5	80.17	6.62	83
1	81.07	6.01	74
2	77.42	6.11	79
3	78.08	6.87	88

The results are plotted in Fig. 1. The curves representing the effect of sodium chloride all proceed to a minimum and show an upward trend similar to the results Wilson and Kern found with magnesium chloride. In all cases sodium sulfate shows greater inhibiting action than sodium chloride, and a minimum with upward slope is obtained only where the liquor is very concentrated. Contrasted to the effect of the electrolytes, we find that sucrose apparently has no effect except at 4 *M* concentration.

TABLE IV (15.5 G. Cr_2O_3 PER LITER)

Concentration of Sucrose M	Protein Per cent	Cr_2O_3 Per cent	Mg. Cr_2O_3 per G. Hide Substance
0	77.47	8.92	115
1	74.76	8.59	115
2	74.72	8.59	115
3	74.83	8.60	115
4	76.74[1]	8.13	106

[1] This sample appeared to be scorched in spots after drying at 100° C.

TABLE V (LIQUORS CONTAINED 15.5 G. Cr_2O_3 PER LITER)

Concentration of Salt M	Log C_{H^+} of Original Liquor	Log C_{H^+} of Filtrate
0	−2.78	−2.90
1	−2.54	−2.67
2	−2.39	−2.43
3	−2.20	−2.33
4	−2.10	−2.20
(Na_2SO_4)		
0	−2.80	−2.85
1	−2.91	−2.92
2	−2.91	−3.07
3	−2.67	−3.01

INTERPRETATION OF RESULTS

Since sucrose hydrates in aqueous solution, the inhibition of the fixation of chrome by the lower concentrations of sodium chloride and of sodium sulfate does not appear to be due to hydration. The writers believe that, as Wilson and Kern suggested for sulfates, sodium chloride, as well as the sulfate, forms addition compounds with the constituents of chrome liquor, rendering them less dissociated and consequently less active in combining with the proteins of hide substance. This is like the influence of sodium chloride in inhibiting the adsorption of mercuric chloride by charcoal, which Rona and Michaelis[12] point out is similar to the decrease in toxicity of mercuric chloride in the presence of sodium chloride. They ascribe such effect to the formation of the complex ions $HgCl_3^-$ and $HgCl_4^=$.

Upon increasing the concentration of salt the hydration effects a virtual concentration of the chrome to such an extent that the retarding action of the addition compound formation is counterbalanced somewhat by the activity of the high chrome concentration, and the curves slope upward. Sodium sulfate does not show the upward slope because, first, owing to mass action it can drive back the ionization of chromic sulfate which represses the activity, as well as causing addition-compound formation, and, second, according to the results of H. C. Jones, it does not hydrate to a large extent. The upward trend with sodium sulfate is shown only where the liquor is very concentrated at the beginning. That the effect of hydration is secondary to addition compound formation is illustrated by sucrose. While it hydrates in aqueous solution, it has no retarding effect on the fixation of chrome. It would seem that since it does not retard the action of the chrome, it must not form the addition compounds, except at concentrations over 3 *M*. The 4 *M* value shows a retardation which we ascribe to a different chemical mechanism. The effect of compounds with several hydroxy groups in forming soluble un-ionizable complexes with the metals, such as tartrate with copper, mannite and glycerol with iron, etc., is well known. The 4 *M* sucrose chrome solution was thick and sirupy in consistency and it seems plausible that a similar compound of chromium and sucrose was formed.

ACKNOWLEDGMENT

We take pleasure in expressing our indebtedness to Messrs. A. F. Gallun and Sons Co., of Milwaukee, for their generous support of this investigation.

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[12] *Biochem. Z.*, **97** (1919), 85.

Industrial Alcohol

During the past few months the securing of alcohol for legitimate manufacturing purposes has been made more difficult and new regulations or modifications of existing ones have placed hardships upon those entitled to tax-free use of this necessary chemical raw material. Many protests have been made and the time has now come when manufacturers must be heard and their claims recognized.

The American Chemical Society at the Rochester Meeting appointed a Committee on Industrial Alcohol with the following personnel: R. F. Bacon, Charles Baskerville, F. R. Eldred, Edward Mallinckrodt, Jr., G. D. Rosengarten, M. H. Ittner, *Chairman*, B. R. Tunison, *Secretary*.

This Committee is anxious to know of any and all cases where legitimate manufacturers have had difficulty in obtaining alcohol needed for industrial purposes, and urges that all details available be sent to it. The Committee is ready to coöperate in every way possible and proposes to place the facts before the authorities in Washington in an effort to have them distinguish between beverage and industrial alcohol and to have them carry out the mandatory provisions of the Prohibition Act, which provides not only for national prohibition, but for the extension and development of the use of alcohol in fuels, dyes, medicinal and pharmaceutical preparations, and other lawful industries.

Correspondence should be addressed to any member of the Committee, but preferably to the Secretary, B. R. Tunison, U. S. Industrial Alcohol Co., 27 William St., New York.

Energy Absorbing Capacity of Vulcanized Rubber[1]

By H. P. Gurney and C. H. Tavener

Boston Belting Co., Boston, Massachusetts

It is the purpose of this paper to indicate some relations which exist between the capacity of vulcanized rubber to absorb or to store up in a potential form and partially to transform or degrade kinetic energy into heat when subjected to single or repeatedly applied stresses, and factors of construction, such as type of crude rubber, rubber content, and particularly the temperature and duration of cure or heat treatment.

Lieut. J. C. Hunsaker[2] has pointed out that airplane shock absorbers are more serviceable when constructed of a high rubber content product than of a low rubber content product (by compounding with larger amounts of mineral fillers). While the energy absorbed in the first stress cycle to which the shock absorber is subjected when an airplane lands is not so great where the rubber content is high, the rate of diminution in successive cycles is not so rapid. To express this in terms of human qualities, a product of high rubber content possesses more endurance and is less rapidly fatigued. The importance of these considerations lies in the fact that the greatest stresses which occur to the airplane structure depend upon the rate of stress increase per unit of energy input into the material which absorbs the landing shocks.

When an airplane lands, there is imposed upon the shock absorbers, an intermittent oscillation of stresses between a minimum and decreasing maxima. In the first cycle, the entire downward energy component of the airplane is largely absorbed as work of extension in the shock absorbers. Immediately following the extension, the absorbed potential energy partly reconverted into an upward kinetic energy component, causing the airplane to bound upward from the earth. On the next return to earth, most of the energy of contraction of the first cycle reappears as energy of extension of the second cycle, minus, of course, whatever portion of this energy has been lost through air friction, and through hysteresis in the tires.[3]

An ideal machine for observing the operation of airplane shock absorbers would measure not only the load-extension relation but, by means of some integrating device, the amount of energy absorbed and returned in successive cycles. By making the energy of extension of any cycle equal to (or a large fraction of) the energy of contraction of the previous cycle, a very accurate comparison could be made between the energy absorbing capacities of different shock absorbers.

Method and Calculations

In the present investigation, samples of vulcanized rubber 0.1 in. thick, 0.5 in. wide, with marks placed initially 2 in. apart, were subjected to different types of fluctuating stresses in a calibrated tensile testing machine, so arranged that loads are recorded both when decreasing or increasing. Recorded strains were read to the nearest 0.1 in. and divided by 2 to convert into extension ratios. To convert loads into stresses, they were divided by the width and thickness of the samples, the widths being measured in 0.01 in. and the thickness in 0.001 in. Thus, approximately, loads multiplied by 20 gave stresses in lbs. per sq. in. All stresses therefore are expressed in lbs. per sq. in. of initial or undistorted cross section unless otherwise noted. The extensions under stress are expressed as the ratio of length under stress to initial or undistorted length under no stress. Under zero stress, the extension is 1 and increases up to the point of rupture, when the stress is called the tensile strength. Instead of basing the tensile upon the initial cross section it may be based upon the cross section of the sample when rupture occurs. This type of tensile is computed by multiplying the tensile based on initial cross section by the extension at break. Owing to the fact that the volume of the sample increases under stress, the assumption involved here, that the cross section and extension are inversely proportional, is only approximately correct. However the increase in volume is due to vacuoles distributed throughout the product adjacent to the mineral particles, and if we disregard these the method of estimating the tensile per cross section at rupture is correct. If the tensile based on the actual cross section at rupture be divided by the proportion of rubber by volume, the resulting tensile thereby becomes based on the actual rubber cross section at rupture. Even this does not take into account micro-inequalities of stress in the rubber portion. These undoubtedly vary from point to point and are doubtless due to the nature, size, concentration, and degree of dispersion of the filling media.

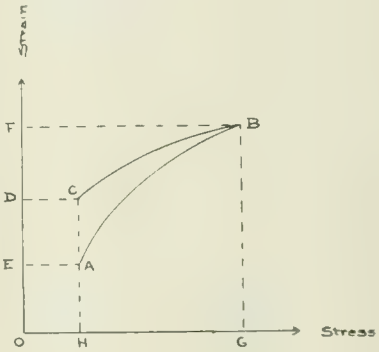

Fig. 1

The work or energy involved in stressing is referred to a unit volume (hence will have the same dimensions as stress). This unit of energy per unit volume is expressed in ft. lbs. per cu. in. This work or energy is of three types.

1—The work of extension, which is the work done upon the vulcanized rubber in increasing the stress from a minimum value to a maximum, whereby kinetic energy is converted into potential energy of stress.

2—The work of contraction, which is the energy released as the stress is reduced from the maximum to minimum value, whereby a portion of the potential energy of stress reappears as kinetic energy.

3—The energy of hysteresis, which is the difference between the energy of extension and contraction.

This may be made clearer by referring to Fig. 1. The condition of the vulcanized rubber is represented by A, the stress being OH or EA, the elongation (extension minus unity) by OE or HA. Let the elongation be increased from OE to OF by an increase of stress of OH to OG. The amount of work done upon a unit volume of rubber by this change is proportional to the area ABFE, since

$$\text{Energy of extension} = \int_{E}^{F} (\text{Stress varying EA to FB}) \times (\text{Infinitesimal strain increases}) = \text{ABFE}.$$

If, thereupon, the stress be reduced from OG to OH, the elongation is not reduced from OF to OE but from OF to OD. The energy liberated is proportional to the area CBED.

$$\text{Energy of contraction} = \int_{F}^{D} (\text{Stress varying FB to CD}) \times (\text{Infinitesimal strain decreases}) = \text{CBFD}$$

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[1] Received July 13, 1921.

[2] "Notes on Aeroplane Shock Absorbers of Rubber," *Aviation and Aeronautical Eng.*, September 1, 1916.

[3] This matter is amply treated from a standpoint of practical design by Prof. A. Klemin, in "Course in Aerodynamics and Airplane Design," in *Aviation and Aeronautical Eng.*, June 1, 1917.

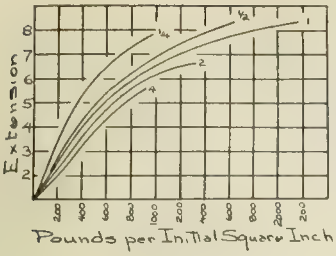

FIG. 2

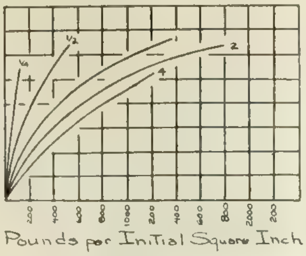

FIG. 3

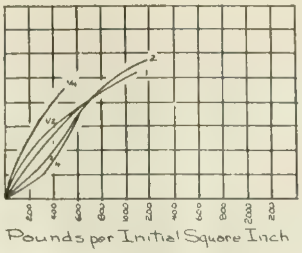

FIG. 4

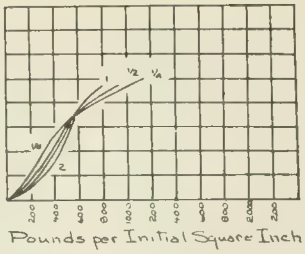

FIG. 5

RELATION BETWEEN STRESS AND STRAIN

Fig. 2—Compound A, cured 0.25 to 4 hrs. at 300° F
Fig. 3—Compound B, cured 0.25 to 4 hrs. at 300° F.
Fig. 4—Compound C, cured 0.25 to 4 hrs. at 280° F.
Fig. 5—Compound C, cured 0.25 to 2 hrs. at 300° F

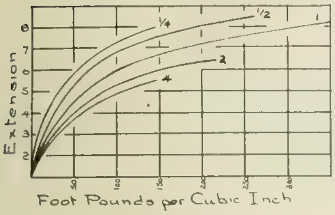

FIG. 6

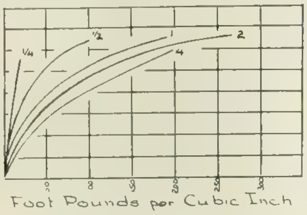

FIG. 7

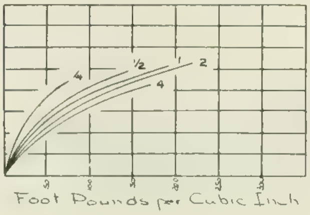

FIG. 8

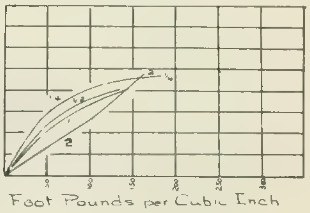

FIG. 9

RELATION BETWEEN STRAIN AND ENERGY ABSORBED PER UNIT VOLUME

Fig. 6—Compound A, cured 0.25 to 4 hrs. at 300° F.
Fig. 7—Compound B, cured 0.25 to 4 hrs. at 300° F.
Fig. 8—Compound C, cured 0.25 to 4 hrs. at 280° F.
Fig. 9—Compound C, cured 0.25 to 2 hrs. at 300° F.

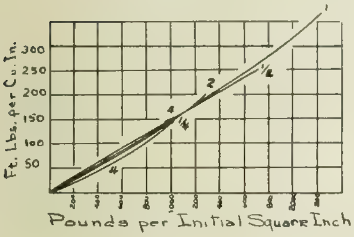

FIG. 10

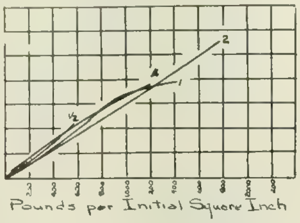

FIG. 11

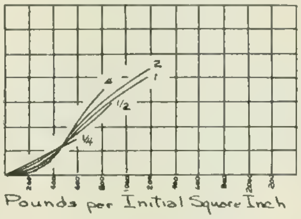

FIG. 12

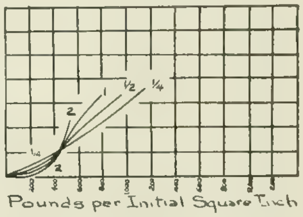

FIG. 13

RELATION BETWEEN ENERGY ABSORBED PER UNIT VOLUME AND STRESS

Fig. 10—Compound A, cured 0.25 to 4 hrs. at 300° F.
Fig. 11—Compound B, cured 0.5 to 4 hrs. at 300° F.
Fig. 12—Compound C, cured 0.25 to 4 hrs. at 280° F.
Fig. 13—Compound C, cured 0.25 to 2 hrs. at 300° F.

The difference between the energy of extension and the energy of contraction is the energy of hysteresis and is proportional to the area ABCDE.

$$ABFE - CBFD = ABCDE$$

If the sample starts from zero stress the points O, A, and E coincide and the energy of hysteresis is proportional to the area ABC. In all work involved in this paper the stress-strain curves were plotted on coördinate paper and the energies of extension and hysteresis determined by planimetering the areas involved and multiplying by a suitable constant.

Referring again to Fig. 1, another cycle may start at C and the process be repeated. The corresponding curves and areas will differ on each successive cycle, although they may approach asymptotically toward definite values and loci.

For the investigation three rubber compounds were employed using a wide range of cures or heat treatments. Compounds A and B in Table I were commercially designated as pure gum stocks, while C was a "compounded" stock. The only difference between A and B was that Plantation Smoked Sheet was used in A, while Upriver Fine Para was used in B. B and C differed in rubber content. In all compounds the ratio of sulfur to rubber was 7 per cent by weight.

Since difference in working has a marked influence upon stress-strain curves, particularly where the stock is heavily compounded, all the mixing and milling of the three compounds took place under as nearly as possible identical conditions and all of each compound was sheeted out at the same time. Even the temperature of breakdown has a bearing; the colder the temperature, the more intense the breakdown effect. Hence as far as possible the temperature during the mixing and milling was kept as uniform as possible throughout.

TABLE I—PROPORTIONS OF INGREDIENTS AND PROPERTIES OF COMPOUNDS
(On volume basis, in parts per thousand)

INGREDIENTS	COMPOUNDS A	B	C
Crude rubber: Fine Para	0	940	0
Smoked sheet	940	0	630
Vulcanizer: Sulfur	30	30	20
Accelerator: Magnesia	10	10	10
Fillers: Whiting	0	0	320
Carbon black	20	20	20
Specific gravity	1.00	1.00	1.52
Per cent of rubber by weight	87	87	38
Ratio of sulfur to rubber by weight	7	7	7
Estimated specific volume heat	0.4	0.4	0.45

Compounds A, B, and C were each cured for 0.25, 0.5, 1, 2, and 4 hrs. at 300° F. In addition, Compound C was cured for the same durations of time at 280° F. In all figures the curves obtained from these cures are designated by the numbers $^1/_4$, $^1/_2$, 1, 2, and 4.

The behavior of these vulcanized rubber samples to stresses will be treated in two general ways, (1) stress increasing from zero to rupture, and (2) stress alternating between definite maxima and minima.

Throughout the work no sample was subjected to more than one test. All samples were allowed to rest several weeks before any tests were started and each series of tests where comparisons are made were performed on the same afternoon.

Table II—Relation between Stress and Energy Absorption

Compound	Temperature Cure ° F.	Hours of Cure	Lbs. per Sq. In. per Ft. Lb. per Cu. In.													
			20	30	40	50	60	70	80	90	100	110	120	130	140	150
A	300	0.25	7.0	6.7	6.5	6.4	6.5	6.6	6.6	6.7	6.8	6.9	7.0	7.1	7.0	...
		0.5	8.5	7.3	7.0	6.8	6.5	6.5	6.3	6.2	6.4	6.3	6.4	6.6	6.6	6.7
		1	8.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	6.8	6.8	6.8	6.8	6.7	6.7
		2	9.0	8.7	8.0	8.0	7.9	7.7	7.5	7.3	7.3	7.1	7.0	6.9	6.7	6.6
		4	12.5	10.7	9.7	9.0	8.3	8.0	7.8	7.6	7.3	7.1	7.0	7.0	...	...
B	300	0.25	7.5	...	...	...	...	...	...	...	...	...	...	...	...	...
		0.5	8.0	7.3	7.0	6.6	6.7	6.4	6.3	5.9	...	...	...	...	...	...
		1	9.9	9.7	8.8	7.6	7.2	7.0	6.8	6.7	6.6	6.4	6.4	6.2	6.0	5.9
		2	10.0	9.8	8.7	8.2	7.8	7.0	7.3	7.1	7.0	6.9	6.8	6.8	6.8	6.7
		4	6.5	6.0	6.8	5.6	5.7	5.6	5.5	5.4	5.5	5.6	5.7	5.8	5.9	6.0
C	280	0.25	10.0	9.7	9.0	8.8	8.3	...	...	...	...	...	...	...	...	...
		0.5	12.0	10.7	9.2	8.8	8.3	7.6	7.3	7.1	6.9	...	...	...	...	...
		1	13.0	11.0	9.5	8.8	8.3	7.4	7.1	6.8	6.5	...	...	...	...	...
		2	15.0	12.0	10.0	9.0	7.7	6.9	6.4	6.0	5.7	...	...	...	...	...
		4	18.0	13.4	10.7	9.0	7.7	6.6	5.9	5.7	5.4	...	...	...	...	...
	300	0.25	13.5	10.7	9.5	8.6	8.0	7.7	7.5	7.3	7.1	...	...	...	...	...
		0.5	15.0	11.7	10.8	8.6	7.7	7.0	6.4	6.0	5.9	...	...	...	...	...
		1	16.5	13.0	10.5	8.8	7.5	6.6	6.1	5.8	5.6	...	...	...	...	...
		2	18.0	13.0	10.9	8.0	6.8	6.1	5.6	5.2	5.0	...	...	...	...	...
		4	...	...	...	...	...	...	...	...	...	...	...	...	...	...

STRESS-STRAIN ENERGY RELATIONS FROM ZERO STRESS TO RUPTURE

The stress-strain curves of all compounds for all cures are plotted in Figs. 2, 3, 4, and 5. Points to be noted are:

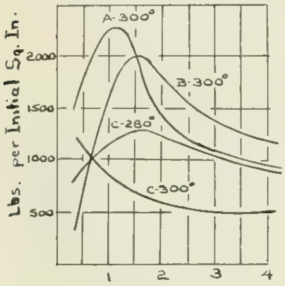

FIG. 14—RELATION BETWEEN STRESS AT RUPTURE AND TIME OF CURE

1—Plantation Smoked Sheet is quicker curing and produces stiffer curves than Fine Para (Figs. 2 and 3).

2—For slight stresses the compounded stock C is stiffer than the purer stocks A and B (Figs. 2 and 4).

3—Higher curing temperature produces greater stiffness (Figs. 4 and 5).

4—In compounded stock C there is a tendency for the curves to intersect (Figs. 4 and 5). Since this work was carried out (1917) one of us has met with this same tendency repeatedly in compounds of about the same rubber content, particularly where overmilling was known to have taken place. The phenomena may have some relation to the softening tendency noted by Gurney in an earlier paper.[4]

The relations between the extension ratio and ft. lbs. per cu. in. are plotted in Figs. 6, 7, 8, and 9. Points to be noted are:

1—A general resemblance to Figs. 2, 3, 4, and 5 except for the absence of a point of intersection.

2—Plantation Smoked Sheet shows less extension for the same energy absorption than Fine Para (Figs. 6 and 7).

3—Stocks A and B are more extensible for equal energy absorptions than the compounded stock C (Figs. 6 and 8).

The relations of stress to energy absorption are plotted in Figs. 10, 11, 12, and 13. The following may be noted:

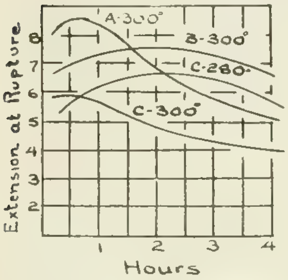

FIG. 15—RELATION BETWEEN STRAIN AT RUPTURE AND TIME OF CURE

1—The relation for A and B is nearly linear for all cures (Figs. 10 and 11).

2—With compounds A and B the direction of slope is nearly constant and independent of the time of cure.

3—With compounded stock C for a given energy absorption:

a—For low energy absorption the stress is greater the longer the cure.

b—For high energy absorptions the stress is lesser the longer the cure. (Figs. 12 and 13.)

4—As a corollary to the above there is a point of intersection or reversal of curvature.

In Table II are given the relations between stress per unit energy absorption and energy absorption for the different compounds and the different cures.

The relations between stresses based on initial, actual, and rubber cross sections, extensions, and energy absorption at rupture and the durations of cure are brought out in Figs. 14, 15, 16, 17, and 18. Except for the curve of Compound C cured at 300° F., these curves exhibit distinct with maxima respect to duration of cure.

Fig. 17 shows that when the tensile is based upon the rubber cross section at rupture there is a tendency toward equalization. The real rupturing strength of the rubber itself is not so markedly reduced by compounding as would be expected.

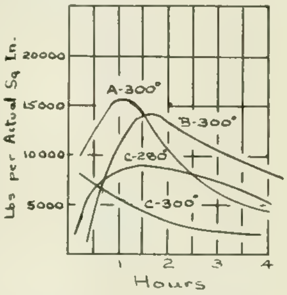

FIG 16—RELATION BETWEEN STRESS AT RUPTURE BASED ON ESTIMATED CROSS SECTION AND TIME OF CURE

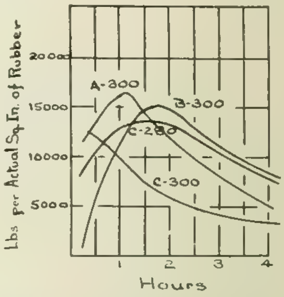

FIG. 17—RELATION BETWEEN STRESS AT RUPTURE BASED ON ESTIMATED RUBBER CROSS SECTION AND TIME OF CURE

ENERGY ABSORPTION AND HYSTERESIS UNDER RECURRING ALTERNATION OF STRESSES

Preliminary to the main portion of this investigation, one compound, A, cured 1 hr. at 300° F. was subjected to alternating stresses between 0 and 300, 600, and 900 lbs. per sq. in.; 100 and 400, 700, and 1000 lbs. per sq. in.; 200 and 500, 800, and 1100 lbs. per sq. in. These stresses therefore commence at 0, 100, and 200 lbs. per sq. in. and increase by 300, 600, and 900 lbs. per sq. in.

In Figs. 19, 20, and 21 are given the extensions at maximum (solid lines) and minimum (dotted lines) plotted against the number of the cycle. The following is apparent:

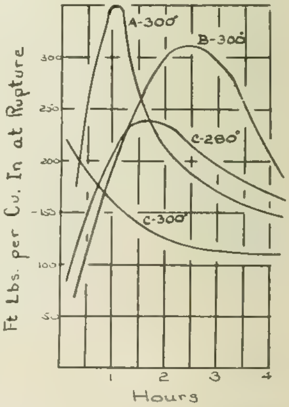

FIG. 18—RELATION BETWEEN ABSORBED ENERGY PER UNIT VOLUME AT RUPTURE AND TIME OF CURE

1—The minimum extensions not only increase as the minimum stress increases, but spread further apart.

2—The maximum extensions increase, although but slightly compared to the minimum extensions.

3—The lines thus plotted are not straight lines although approaching asymptotically to a straight line.

Figs. 22, 23, and 24 exhibit energy absorption (solid lines)

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[4] THIS JOURNAL, **13** (1921), 707.

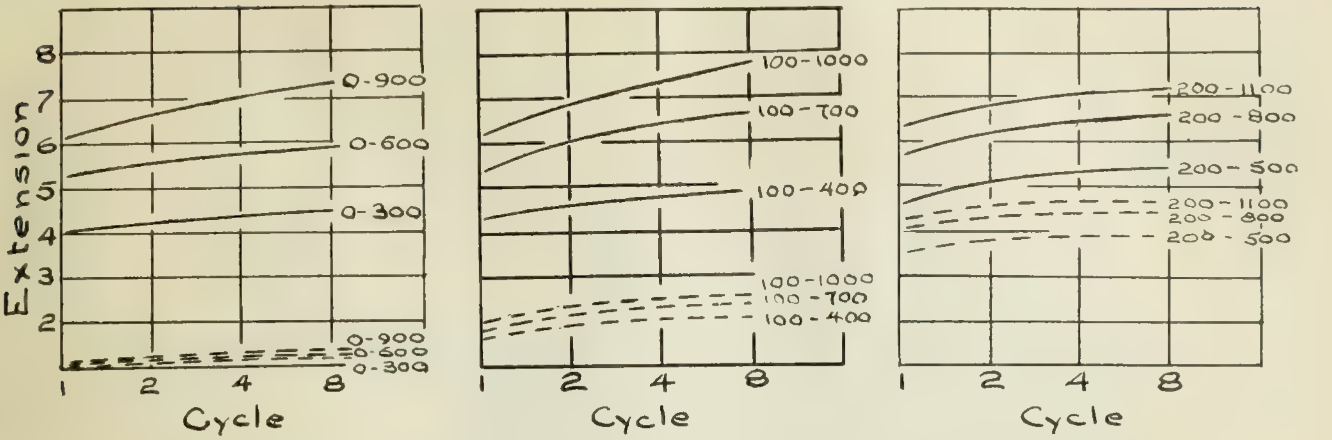

Fig. 19 Fig. 20 Fig. 21

Relation between Cycle Number and Maximum and Minimum Extensions, Compound A, Cured 1 Hr. at 300° F.

Fig. 19—Stresses alternating between 0 and 300, 600, and 900 lbs. per sq. in. Fig. 20—Alternating between 100 and 400, 700, and 1000 lbs. per sq. in. Fig. 21—Alternating between 200 and 500, 800, and 1100 lbs. per sq. in.

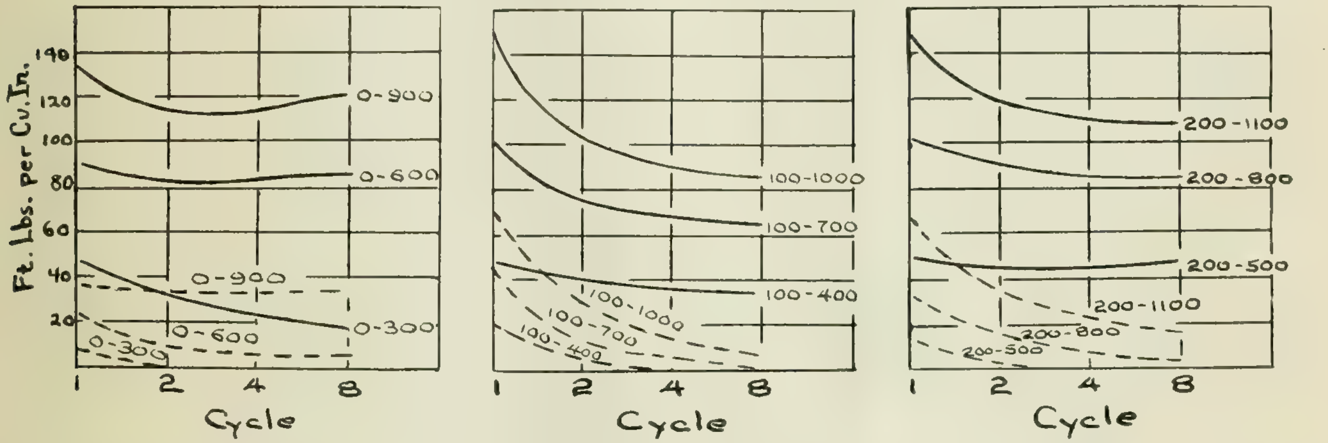

Fig. 22 Fig. 23 Fig. 24

Relation between Cycle Number and Maximum (Solid Lines) and Hysteresis (Dotted Lines) Energy per Unit Volume, Compound A, Cured 1 Hr. at 300° F.

Fig. 22—Stresses alternating between 0 and 300, 600, and 900 lbs. per sq. in. Fig. 23—Alternating between 100 and 400, 700, and 1000 lbs. per sq. in. Fig. 24—Alternating between 200 and 500, 800, and 1100 lbs. per sq. in.

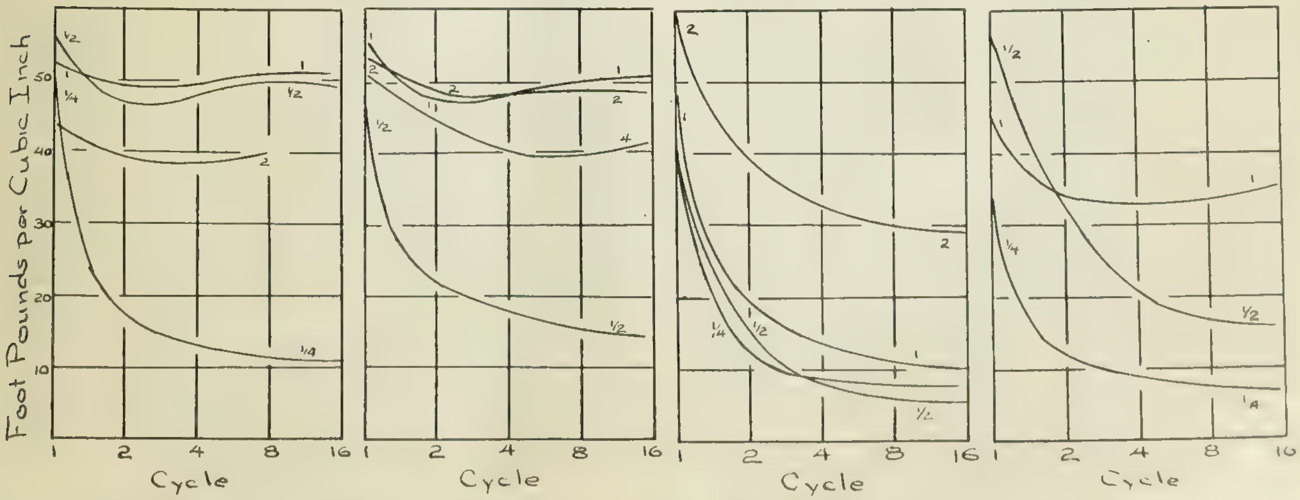

Fig. 25 Fig. 26 Fig. 27 Fig. 28

Relation between Cycle Number and Maximum Energy Absorbed per Unit Volume, Stresses Alternating between 100 and 400 Lbs. per Sq. In.

Fig. 25—Compound A, cured 0.25 to 2 hrs. at 300° F.
Fig. 26—Compound B, cured 0.5 to 4 hrs. at 300° F
Fig. 27—Compound C, cured 0.25 to 2 hrs. at 280° F.
Fig. 28—Compound C, cured 0.25 to 1 hr. at 300° F.

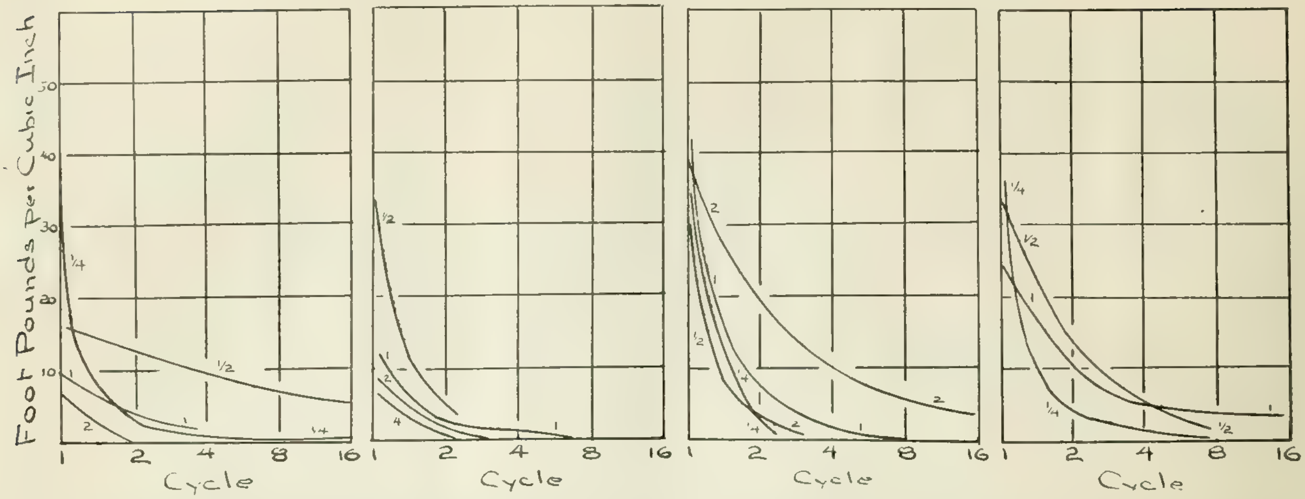

Fig. 29 Fig. 30 Fig. 31 Fig. 32

Relation between Cycle Number and Hysteresis Energy per Unit Volume, Stresses Alternating between 100 and 400 Lbs. per Sq. In.

Fig. 29—Compound A, cured 0.25 to 2 hrs. at 300° F.
Fig. 30—Compound B, cured 0.5 to 4 hrs. at 300° F.
Fig. 31—Compound C, cured 0.25 to 2 hrs. at 280° F.
Fig. 32—Compound C, cured 0.25 to 1 hr. at 300° F.

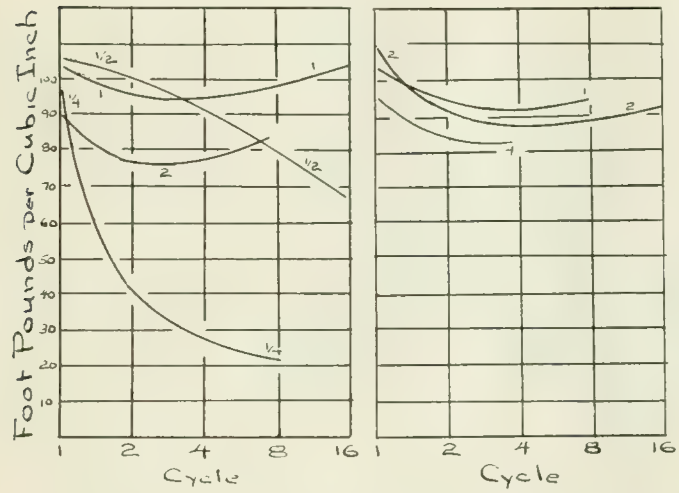

Fig. 33 Fig. 34

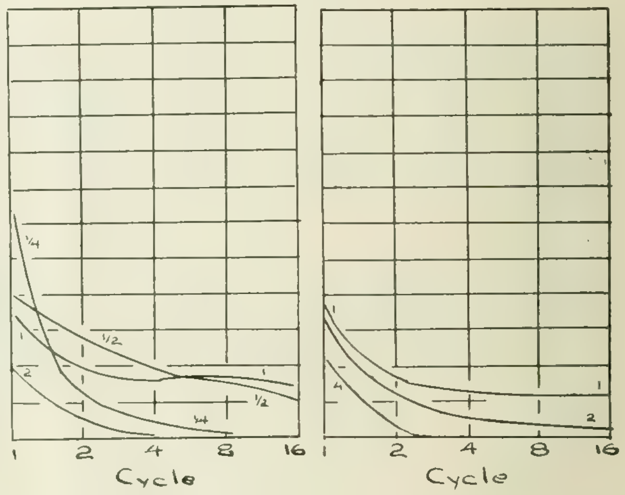

Fig. 35 Fig. 36

Relation between Cycle Number and Maximum Energy Absorbed per Unit Volume, Stresses Alternating between 100 and 700 Lbs. per Sq. In.

Fig. 33—Compound A, cured 0.25 to 2 hrs. at 300° F.
Fig. 34—Compound B, cured 1 to 4 hrs. at 300° F.

Relation between Cycle Number and Energy of Hysteresis per Unit Volume, Stresses Alternating between 100 and 700 Lbs. per Sq. In.

Fig. 35—Compound A, cured 0.25 to 2 hrs. at 300° F.
Fig. 36—Compound B, cured 1 to 4 hrs. at 300° F.

and energy of hysteresis (dotted lines) plotted against cycle number. This brings out the following facts:

For equal stress differences between maximum and minimum the hysteresis loss is: (1) Greater on the first cycle for high minimum stress; (2) declines more rapidly with increasing cycles as the minimum stress increases.

This makes it clear that where hysteresis is a desirable property, as in airplane shock absorbers, the minimum stress should be low. Reinforcing this is the fact that a state of strain accelerates the aging or depreciation of rubber goods.

Adopting as standard, stresses alternating between 100 and 400 lbs. per sq. in. and applying this to most of the samples, energy absorptions are plotted against cycle numbers in Figs. 25, 26, 27, and 28, while the hysteresis energy is plotted in Figs. 29, 30, 31, and 32. From these curves the following points are apparent:

1—The energy absorbing capacity at maximum stress is greater for pure gum stocks A and B than for compounded stock C (Figs. 25 and 26 *vs.* 27 and 28).

2—The effect of increasing the duration of cure may be divided into two phases:

a—From low cure to an intermediate optimum or moderate cure there is an initially high hysteresis, decreasing rapidly as the number of the cycle advances, this stage becoming modified with longer cure to lower values of hysteresis on first cycle, but better sustained on later cycles.

b—From an intermediate optimum or moderate to long cure the hysteresis is uniformly lowered for all cycles.

Another way of putting this is that on the first cycle the hysteresis is greater for shorter cures, but in later cycles the hysteresis increases, passes through a maximum and then decreases as the duration of cure is extended.

Figs. 33, 34, 35, and 36 bring out essentially the same facts where the minimum stress is 100 and the maximum stress is 700 lbs. per sq. in.

The maxima in Fig. 18 give the greatest number of ft. lbs. per cu. in. that these compounds can absorb without rupturing. If these amounts are converted into equivalent heat units and confined adiabatically to the rubber, the rises in temperature would be as indicated in Table III.

Table III

Compound	Maximum Ft. Lbs. per Cu. In.	Specific Volume Heat	Rise in Temperature ° F.
A	350	0.4	31
B	310	0.4	28
C	240	0.45	19

CONCLUSIONS

1—Fine Para possesses no distinct advantage over plantation rubber so far as tensile capacity, speed of cure, or hysteresis endurance are concerned.

2—Excess cure produces lower hysteresis on all cycles than more moderate cure.

3—Under cure produces greater hysteresis on the first cycle, but more rapid decay on following cycles than moderate cure.

4—The chief advantages of a pure gum stock lies not in a higher hysteresis on the first cycle but in:

a—Greater capacity to absorb energy prior to rupture.

b—Superior hysteresis endurance.

c—Greater rate of extension per rate of energy absorption, hence transfer of energy from airplane to shock absorbers and reverse is slower, thereby setting up lesser stresses in the airplane.

The Solubility of Gases in Rubber and Rubber Stock and Effect of Solubility on Penetrability[1,2]

By Charles S. Venable and Tyler Fuwa

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

The recent rapid development of rubberized balloon fabric has led to an extensive study of the penetration of gases through rubber and the various factors influencing this penetration. Edwards and Pickering[3] have shown that for any one gas the rate of penetration through a given sample of rubber is directly proportional to the partial pressure difference and increases rapidly with the temperature. The relative penetrability values obtained by them for various gases are in good agreement with similar values determined by Graham[4] and Dewar.[5] Comparable results were also obtained by Daynes.[6] Since there was no apparent relationship between relative penetrability and density of the gas, Graham postulated that the penetration mechanism consisted in the solution of the gas on one side of the rubber, with a subsequent diffusion of the dissolved gas through the rubber and vaporization on the other side. Later investigators are inclined to take the same view.

Though penetrability is thus made a function of the solubility of the gas in the rubber, the mathematical relationship has been indeterminate on account of the lack of accurate solubility data. By weighing sheets of rubber after exposure to the gas, Wroblewski[7] obtained rough solubility data for nitrous oxide, carbon dioxide, hydrogen, and air. Values were also given for temperature coefficients but all his results were subject to very large experimental error. Hüfner[8] states that between 0° and 25° C. a gray vulcanized rubber stopper in an atmosphere of carbon dioxide absorbs about its own volume of the gas. He finds no absorption for hydrogen and nitrogen, and no absorption for oxygen beyond that involved in oxidation of the rubber. From a study of equilibrium pressures for a known volume of gas in contact with the rubber, Reychler[9] determined the solubility at 18° C. of carbon dioxide at 1.06 volumes and sulfur dioxide at 26 volumes per volume of rubber.

Recently Daynes,[6] by measuring the "lag" or time consumed in saturating the rubber membrane in the Shakespear permeameter, has attempted to separate the permeability coefficient into its absorption or solubility coefficient and its diffusion coefficient. He worked with hydrogen, carbon dioxide, nitrous oxide, air, oxygen, and ammonia, but his results are open to the criticism that the "lag" period measured must have a relatively large correction applied for instrument lag. His interpretation of results is also somewhat vitiated by curious errors in density values assumed (page 305).

Recently this Laboratory, in connection with an investigation undertaken for the Goodyear Tire & Rubber Co., has been making a study of the solubility of gases in rubber and rubber stock, using a direct experimental procedure capable of giving more accurate results than any hitherto published.

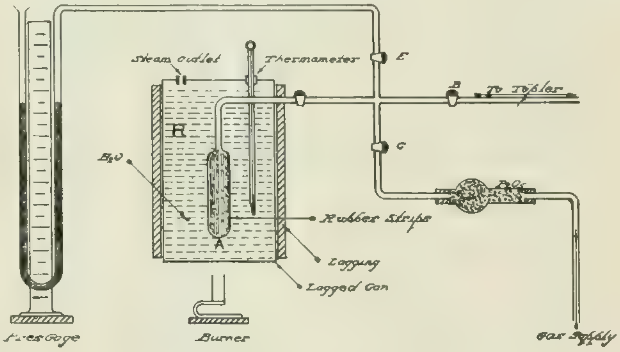

FIG. I—APPARATUS FOR DETERMINING SOLUBILITY OF GAS IN RUBBER

EXPERIMENTAL PROCEDURE

The procedure consisted essentially in leaving thin strips of rubber, from which all dissolved gas had been removed by evacuation, in contact with an atmosphere of the gas under the conditions desired until equilibrium was established. This gas was then pumped out with a Töpler pump and measured over mercury, due correction being made for the void gas in the container system used. This procedure, therefore, in contrast to those previously attempted, allows a direct determination of the volume of gas held in free condition by the rubber.

The apparatus is shown in Fig. I. A weighed amount of rubber cut into thin strips was placed in the glass bulb A. Connections were made through C with a tube by which the gas (dried over P_2O_5 or soda lime) could be introduced into the bulb. By means of stopcock B connection was made with a Töpler pump and by means of E with a mercury manometer. A large water reservoir, R, around the bulb served as the means of temperature control.

After the apparatus had been carefully tested for leaks, the rubber was placed under high vacuum for 48 hrs. to exhaust all dissolved gases. Preliminary experiments demonstrated that for the thickness of rubber used, and at room temperature, 24 hrs. were required for equilibrium to be

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[1] Presented before the Division of Rubber Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Contribution No. 38 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] *Chem. Met. Eng.*, **23** (1920), 17, 71.

[4] *Phil. Trans.*, **156** (1866), 399.

[5] *Proc. Roy. Inst., Gt. Britain*, **21** (1915), 558, 813.

[6] *Proc. Roy. Soc. London*, **97A** (1920), 286.

[7] *Wied. Ann. Phys.*, **8** (1879).

[8] *Ibid.*, **34** (1888), 1.

[9] *J. chim. phys.*, **8** (1910), 39, 617.

established in the case of all gases save ammonia and sulfur dioxide; at 100° C., only 2 hrs. were required. A corresponding time was used for pumping out the dissolved gas. The time required for equilibrium for ammonia and sulfur dioxide was about twice that for the other gases.

To determine a solubility value, the evacuated rubber was left in contact with the dry gas under the desired conditions until equilibrium was established, as indicated by the constancy of the pressure in the bulb. Stopcocks C and E were then closed and the gas (void gas and dissolved gas) in the bulb system ABCE was pumped out and measured. The difference between the total volume and void volume represented the dissolved gas. This quantity was calculated over to the basis of cc. gas (N. P. T.) per 100 cc. of raw rubber, or in the case of the compounded samples, cc. gas (N. P. T.) per 100 cc. of rubber actually present in the mix.

DETERMINATION OF VOID VOLUME—From gage readings, it was found that when a gas appreciably soluble in rubber was introduced into the bulb, the initial rate of solution was very rapid. Consequently, the void volume was determined by introducing hydrogen into the bulb system containing the evacuated rubber and at the end of 5 min. pumping it out and measuring the gas. Gage readings during that interval had shown that the volume of hydrogen taken up by the rubber was so nearly zero as to be well within the other experimental errors involved. Confirmation of this very low solubility for hydrogen is shown by the fact that when air was introduced into the bulb system and removed after 5 secs.' exposure, the volume of air obtained (260.3 and 260.6 cc.) was only very slightly greater than the volume of hydrogen removed (260.02 cc.) after 3 hrs.' exposure to the latter gas.

PRECISION—Duplicate determinations showed the whole procedure to have approximately the precision indicated in Table 1.

TABLE 1

(Solubility cc. gas (N. P. T.) per 100 cc. rubber)

Values	Maximum Possible Deviation Per cent
3 to 5	About 40
5 to 10	About 20
10 to 25	About 10
Above 25	About 5

SAMPLES USED

I. *Pale Crepe*—From a lot some 3 or 4 yrs. old.

II. *Smoked Sheet*—Obtained from Akron together with III and IV. It is understood that this same rubber was used in compounding III and IV.

III. *Original Composition* (by wt.)

Smoked sheet	100
ZnO	10
Thiocarbanilide	3
Combined sulfur	3.2% of wt. smoked sheet present

IV. *Original Composition* (by wt.)

Smoked sheet	100
ZnO	10
S	20
Thiocarbanilide	0
Combined sulfur	2.56% of wt. smoked sheet present

Sample IV obviously contains an abnormal amount of free sulfur.

EXPERIMENTAL RESULTS

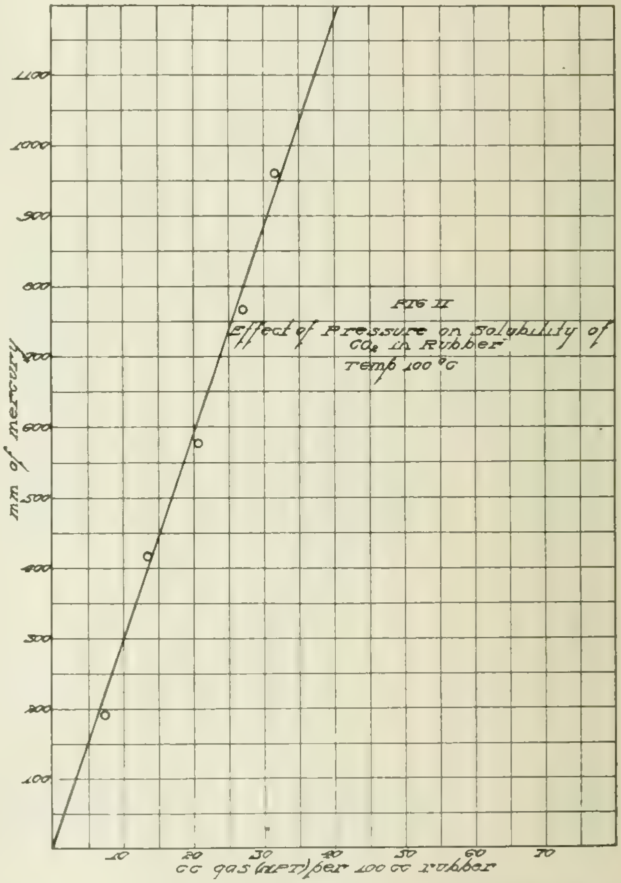
EFFECT OF SURFACE—Solubility Determinations made on a sample of rubber cut so that in Case A the surface exposed was about three times that in Case B, showed that there was no difference in the amount of gas held by the Rubber A and Rubber B. The effect of surface area is apparently negligible so far as final solubility is concerned, indicating that the gas is held in true solution and not by adsorption on the macroscopic surface of the rubber.

SOURCE OF GAS USED

CO_2	Cylinder—97.5 per cent
CO	From Na formate + H_2SO_4
CH_4	From NaAc + NaOH (> 90 per cent)
O_2	Cylinder (> 99 per cent)
H_2	Cylinder (> 98 per cent)
N_2	Cylinder (> 97 per cent)
SO_2	Cylinder
C_2H_4	From alcohol + P_2O_5—(> 90 per cent)
H_2S	From FeS and HCl
NH_3	Cylinder (> 98 per cent)
He	Cylinder from Petrolia, Texas (est. 92 per cent He, 8 per cent N_2)

SAMPLE OF CALCULATIONS

Sample IV. Vulc. coefficient = 2.56 per cent.
Equilibrium for 24 hrs. at room temperature
Wt. sample = 71.1 g. = 54.7 g. rubber = 59.4 cc. rubber
Bulb closed at 23.7° C. and 771.2 mm. Hg
Gas collected (at 23.7° and 771.2 mm.) = 125.9 cc.
Void volume (det. with hydrogen) = 67.2 cc.
Dissolved gas = 58.7 cc. (23.7° C. and 771.2 mm. Hg) = 54.8 cc. (N. P. T.) = 92.2 cc. per 100 cc. rubber



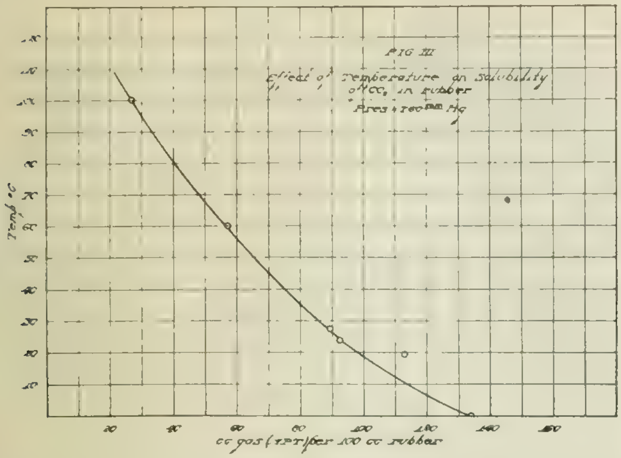
EFFECT OF GRADE OF RUBBER AND VULCANIZATION COEFFICIENT—The effect of the grade of rubber and vulcanization coefficient on the solubility of carbon dioxide at room temperature is shown in Table 2. Since these determinations were made at temperatures ranging from 16° to 24° C., the values were calculated to the common basis of 20° C. by referring to the slope of the curve shown later in Fig. III.

TABLE 2—EFFECT OF GRADE OF RUBBER AND VULCANIZATION COEFFICIENT ON SOLUBILITY OF CO_2 IN RUBBER

Pressure CO_2 = 760 mm. Hg.
Solubility reported in cc. gas (N. P. T.) per 100 cc. initial raw rubber

		SOLUBILITY	
	SAMPLE	Observed	Calculated to 20° C.
I.	Pale crepe (raw)	90 at 21° C.	92
II.	Smoked sheet (raw)	108 at 16° C.	102
III.	Smoked sheet (vulc. coeff. = 2.56)	92 at 24° C.	99
IV.	Smoked sheet (vulc. coeff. = 3.2)	103.5 at 19° C.	101

There is a 10 per cent difference between unvulcanized pale crepe and smoked sheet. On the other hand, when smoked sheet is vulcanized to different coefficients up to 3.2 per cent, there is comparatively little difference between the volume of gas held by 100 cc. of the raw rubber and 100 cc. of the same rubber after vulcanization. The 10 parts of zinc oxide and 17 parts of free sulfur present also appear to exert no appreciable effect on the solubility when the results are calculated on the basis of the rubber present. Accordingly, free use has been made of either Samples III and IV in obtaining solubility data, though the sample used is always indicated.



EFFECT OF PRESSURE—A study was made of the effect of pressure on the solubility of carbon dioxide in rubber. These determinations were made at 100° C., on a sample of rubber from Lot IV. The results are shown in Fig. II.

It will be noted that the solubility is directly proportional to the absolute pressure within the limits investigated. This is additional proof that the gas is held in true solution rather than by adsorption; this evidence rules out the possibility of adsorption even on the surface of the colloidal units of rubber.

EFFECT OF TEMPERATURE—The effect of temperature on the solubility of carbon dioxide in rubber is shown in Fig. III. The rubber was taken from Lot IV, and the pressure was 760 mm. Hg.

The curve is the usual type of solubility curve. Using the solubility equation

$$\frac{d \log S}{d t} = \frac{\Delta H}{RT^2}$$

and plotting log S against $\frac{1}{T}$, the points fall fairly well on a straight line. From the slope of this line, ΔH (the molal heat of solution of carbon dioxide in rubber) is calculated to be about 3300 cal. It will be noted that the solubility at 140° C., or vulcanization temperature, will be very small. In the case of carbon dioxide, the solubility at 100° C. is about one-third that at 20° C. As seen from Table 3, in the case of the other gases the solubility at 100° C. is usually about one-half that at 20°, indicating a lower heat of solution than for carbon dioxide.

RELATIVE SOLUBILITY OF VARIOUS GASES The relative solubility of the various gases in rubber is shown in Table 3. Rubber from Lots III and IV was used. The determinations were made at a gas pressure at 760 mm. Hg and at the temperatures indicated. The critical temperature for each gas is given in degrees Kelvin in Column 5.

As previously explained, the solubility of hydrogen is too low to be determined by the procedure used, and in the above table, it has been indicated simply as less than 1. The same was found to be the case for helium. Comparing solubilities with critical temperatures, the order of the solubility in rubber of the various gases is the same as the order of their absolute critical temperatures, save in the case of the unsaturated ethylene, which indicates that the degree of solubility is roughly proportional to the ease of condensation of the gas.

TABLE 3—SOLUBILITY OF VARIOUS GASES IN VULCANIZED RUBBER

	Solubility cc. gas (N. P. T.) per 100 cc. rubber			
	Sample III	Sample IV		Critical Temperature
GAS	20°–22°	20°–22°	100°	° K.
He	......	<1.0	<1.0	5.0
H_2	<1.0	<1.0	<1.0	33.0
N_2	3.5	.....	1.7	128.3
CO	6.2	.....	3.6	134.4
O_2	7.3	.....	4.0	155.0
CH_4	26.8	24.0	.....	190.2
CO_2	99	101	34.0	304.0
C_2H_4	......	144	66	282.6
H_2S	......	273	.....	373.4
NH_3	930	.....	.....	406.0
SO_2	1950	.....	.....	428

In Table 4 are given comparative values of the solubility of the various gases in rubber and in water at 21° C. The values for water were taken from the Landolt-Börnstein "Tabellen," being largely the figures given by Winkler. In the last column are given the ratios of the solubility in rubber to that in water.

TABLE 4—SOLUBILITY OF GASES IN RUBBER AND IN WATER

Solubility given in cc. gas (N. P. T.) per 100 cc. solvent. Temp.= 21° C.

	Rubber Sample III	H_2O	$\frac{R}{H_2O}$
He	<1.0 (Sample IV)	1.4	<0.7
H_2	<1.0	1.8	<0.6
N_2	3.5	1.5	2.3
CO	6.2	2.24	2.7
O_2	7.3	3.0	2.4
CH_4	26.8	3.2	8.4
CO_2	99	82.9	1.2
C_2H_4	144 (Sample IV)	11.6	12.5
H_2S	273 (Sample IV)	243	1.1
NH_3	930	67,830	0.014
SO_2	1950	3661.7	0.53

In the case of hydrogen and helium, the exact ratio is unknown, but is evidently small. As would be expected, the two hydrocarbons, methane and ethylene, are much more soluble in rubber than in water, whereas ammonia and sulfur dioxide, which form hydrates in aqueous solution, are much more soluble in water than in rubber. In the case of the other gases, the ratio is fairly constant.

RELATIONSHIP BETWEEN RELATIVE SOLUBILITY AND RELATIVE PENETRABILITY

If the process by which a gas penetrates through a rubber membrane is one of the solution of the gas on one side of the membrane, diffusion of dissolved gas through membrane, and evaporation on the other side, inasmuch as Edwards and Pickering[3] have shown that for any one gas the rate of penetration is indirectly proportional to the thickness of the membrane, it can be assumed that this rate of penetration is determined by the second stage of the process, that is, diffusion of dissolved gas. The expression for the rate of penetration of a gas through rubber might thus be expected to take the form:

$$P = k\,D\,C$$

where k = proportionality constant depending upon the condition of the rubber, the temperature, etc.

D = rate of diffusion of an individual molecule,

C = concentration of gas in true solution (not including molecules which are combined chemically so as not to be able to move freely).

As a first approximation, it may be assumed that C is correctly measured by S, the solubility as determined in the previously mentioned experiments, and that D, the rate of diffusion through the rubber, is proportional to the disordered heat motion of the gas molecule, *i. e.*, inversely proportional to the square root of the molecular weight. Thus the equation for rate of penetration becomes:

$$P = K \frac{S}{\sqrt{\text{Mol. Wt.}}} \text{ or } K = \frac{P \times \sqrt{\text{Mol. Wt}}}{S}$$

where P = relative penetrability, S = relative solubility, and K = proportionality factor depending upon the temperature, etc.

In the following discussion, values reported by Edwards[3] have been used, as representing the most recent and probably the most accurate work. Carbon monoxide and methane were not investigated by Edwards and, accordingly, the values given by Dewar[5] and Graham[4] have been taken. This introduces a slight error, inasmuch as the values given by Edwards and Pickering were obtained at 25° C. and those given by Dewar and Graham at 15° C. The figures, however, are for relative penetrability compared to nitrogen and in each case were calculated on the basis of the value given for nitrogen by that particular investigator. Although all gases have not the same temperature coefficient, it is believed that no large error is introduced by assuming the same relative temperature coefficient between 15° and 25°.

In Table 5, eight gases are considered, for which both relative penetrability and relative solubility values (N = 1) are now known. In Column 3 are given values for the term

$$K = \frac{P \times \sqrt{\text{Mol. Wt.}}}{S}.$$

Table 5 shows that for four gases, oxygen, nitrogen, carbon monoxide, and carbon dioxide, whose solubilities vary 28-fold, there is a fair degree of constancy in the values calculated for K considering the fact that the experimental errors involved in the two determinations might be 10 to 30 per cent. The wide variation in the case of the other four gases—hydrogen, helium, methane, and ammonia—indicates, however, that some fundamental error must have been made in the underlying assumptions involved in the equation.

TABLE 5

GAS	Relative Penetrability	Authority	Relative Solubility (at 20°–22° C.)	$K = \frac{P \times \sqrt{\text{Mol. Wt.}}}{S}$	Relative Size of Molecule ($b \times 10^5$)
Helium	4.04	E. & P.	0.3	— 40	70
Hydrogen	6.25	E. & P.	0.3	29.5	119
Nitrogen	1.00	E. & P.	1.00	5.3	174
Carbon monoxide	1.31	Dewar	1.77	3.9	178
Oxygen	2.81	E. & P.	2.09	7.6	144
Methane	2.22	Graham	7.6	1.2	191
Carbon dioxide	18.1	E. & P.	28.3	4.2	191
Ammonia	50.0	E. & P.	266	0.78	165

Now, in deriving the expression for K, it was assumed that the rate of motion through the rubber is proportional only to the disordered heat motion, that is, inversely as the square root of molecular weight. This totally neglects any other factor, such as the relative size or the structure of the gas molecules, which it is quite reasonable to suppose should influence the rate of diffusion through a colloidal solid such as rubber.

In Column 4 are given relative values of molecular volumes as computed from the quantity *b* in van der Waal's equation. Pease[10] has recently shown that these values are in close accord with the Lewis-Langmuir theory. The abnormally high diffusion rate of helium and hydrogen might well be explained on the basis of the relatively small size of gas molecule. Apparently, however, no such relationship holds in the case of the other gases.

If, however, we consider the structure of the molecules from the standpoint of the Langmuir theory, the eight gases readily group themselves into three different classes:

1—Helium and nitrogen, which do not form octets, are considerably smaller than the other gases and would be expected to diffuse more rapidly through a given medium.

2—Oxygen, nitrogen, carbon monoxide, and carbon dioxide form either single octets or octets joined together by their faces with no hydrogen nuclei on the outside. This group should behave quite similarly.

3—Methane and ammonia form two very similar molecules with four and three exposed hydrogen nuclei, respectively, on the outside of the octet. It is quite possible that such molecules would diffuse more slowly through the rubber colloid, especially because the rubber hydrocarbon has a large number of unsaturated linkages.

As regards the effect of temperature, in conducting a diffusion at 100° C. in place of 25° C., the solubility of the gas is decreased by at least one-half. The disordered heat motion (proportional to the square root of absolute temperature) is increased by less than 15 per cent. On the other hand, Edwards and Pickering[3] have shown that at 100° C. the rate of diffusion in the case of carbon dioxide is about six times, and in the case of hydrogen and helium, about seven to eight times that at 25° C.

It is obvious, therefore, that the value for K in the above formula must increase ten- or twelve-fold for a 75° rise in temperature. This is, however, not surprising, for while it is somewhat greater than the change in the rate of diffusion of solutes through water, the order of magnitude is the same, and the coefficient of expansion of rubber is much greater than that for water, and its decrease in "viscosity" would undoubtedly prove correspondingly greater if it could be measured by ordinary methods. The viscosity of heavy oils varies thirty-fold in magnitude over a similar range in temperature.

On the whole, therefore, all the evidence seems to favor the customary assumption that the mechanism by which gas penetrates a rubber membrane is through diffusion of the gas, which is held in true solution. While both the solubility and molecular weight of the gas play their expected part in influencing the speed of diffusion, the size and structure of the gaseous molecule and the viscosity of the rubber itself are additional important factors in determining the precise rate of diffusion. The attempt has been made above to analyze these factors as far as it is possible with the limited amount of data now available, which are admittedly inadequate for positive conclusions.

SUMMARY

1—It has been found that when rubber absorbs a gas, this gas is, in most cases at least, held in true solution and not by adsorption.

2—In the case of carbon dioxide, which has about an average solubility, the amount of gas thus held in true solution by the rubber is, within the limits investigated, directly proportional to the pressure and is unaffected by degree of vulcanization or the presence of compounding ingredients.

3—The solubility decreases rapidly with increasing temperature.

4—Relative solubility values obtained for various gases show that there is a general relationship, such as might be expected on purely theoretical grounds, between the solubility and the density of a gas, and its relative rate of penetration through rubber. The indications are, however, that the actual size and structure of the gas molecule and the viscosity of the rubber likewise markedly influence this rate of penetration, and in a direction which can be predicted.

ACKNOWLEDGMENT

The Laboratory wishes to express its appreciation for the helpful coöperation of the Goodyear Tire and Rubber Company and for their courtesy in permitting the publication of these results.

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[10] *J. Am. Chem. Soc.*, **43** (1921), 991.

Cyanamide in Some Fertilizer Mixtures[1]

By W. S. Landis

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At the meeting of the American Chemical Society in Chicago in 1920, Mr. R. H. Harger, of the United States Department of Agriculture, presented a paper entitled "The Changes Taking Place in Cyanamid when Used with Mixed Fertilizers,"[2] in which he described the behavior of certain experimental mixtures of fertilizer materials and Cyanamid made up in gram lots in the laboratory, and reported after a certain time interval a material decrease in the cyanamide nitrogen content and a corresponding increase in dicyanodiamide nitrogen. The author remarks that this results in a considerable waste of fertilizer nitrogen, and that methods should be evolved to prevent such waste. Fortunately, the facts as stated are not found applicable to standard brands of fertilizer in which cyanamide has been properly incorporated, some studies of which form the basis of this paper.

Observation of the rapid transformation which cyanamide undergoes in fertilizer mixtures, or even when applied alone to the soil, is not new. The decomposition and transformation have been the subject of world-wide investigation, and the principles developed are applied on an ever increasing commercial scale, there being found on the market numerous chemical products, such as ammonia, urea, dicyanodiamide and the guanidines, made from cyanamide, some of them in quantities quite comparable with those obtained from other sources. The general reactions involving these decompositions have been the subject of numerous publications and need not be repeated here.[3]

Returning to the Chicago paper, the author's discovery that the cyanamide nitrogen as such had completely disappeared from fertilizer mixtures in which cyanamide had been used in their formulation, was by no means a new one. In the "American Fertilizer Handbook" for 1914, the transformations taking place in cyanamide in fertilizer mixtures were referred to, this subject having been investigated years before Mr. Harger's experiments.

The surprising feature of Mr. Harger's paper, however, was his conclusion that the decomposition product of the cyanamide in the fertilizer mixture was "represented principally by, and in many cases quantitatively by the formation of dicyanodiamide."[4] According to his experimental results, a mixture of cyanamide and moist acid phosphate containing 22 g. of cyanamide and 184 g. of acid phosphate, to which 16 g. of water were intentionally added, showed that in 8 days practically 90 per cent of the cyanamide nitrogen had been transformed into dicyanodiamide nitrogen.

Now dicyanodiamide is an article of commerce and has been so for many years. Exhaustive studies have been made on its production from cyanamide.[5] A comprehensive review of the suggestions and methods of these investigators made in the laboratory of this company have confirmed most of their findings. By the most efficient method of procedure, coupled with the most exacting laboratory control, we were able to transform about 85 per cent of the cyanamide nitrogen in aqueous solution into dicyanodiamide nitrogen. Since the solubility of cyanamide in water is a difficult and in many cases an inefficient process, the over-all transformation efficiency from cyanamide to dicyanodiamide has always been low. Every investigator in this field has noted the fact that in this transformation only a part of the cyanamide nitrogen goes to dicyanodiamide nitrogen and this fraction seems fairly constant, irrespective of the method of making the transformation, provided such method has good foundation in fact. In large-scale work where quantities of a ton or more are operated on and control is not quite so exact as in the laboratory, our experience has shown that less than five-sixths of the cyanamide nitrogen brought in solution can be transformed into dicyanodiamide nitrogen, and about one-sixth always goes to urea nitrogen. With less exacting control and more nearly paralleling factory conditions, this fraction going to urea nitrogen is materially greater than one-sixth and we consider it good factory practice if it does not exceed one-fourth. It is extremely interesting to find that Mr. Harger's accidental method, which involves no presolution of the cyanamide whatever, should be able to transform cyanamide into dicyanodiamide at a conversion efficiency of about 90 per cent.

EXPERIMENTAL MIXTURES OF ACID PHOSPHATE AND CYANAMIDE

However, more closely to parallel fertilizer conditions, and shortly after the reading of the Chicago paper, one of the large agricultural chemical companies mixed up a batch of commercial acid phosphate and cyanamide in one of its fertilizer factories. The mixture was of the proportion of 1900 lbs. of commercial acid phosphate and 100 lbs. of cyanamide, and the pile was carefully sampled by the agricultural company's chemist. Ten days after mixing (this elapsed time taken to represent periods similar to those reported at Chicago) this sample was tested in the laboratory with the following results: On the addition of picric acid as in the Harger procedure, precipitates were obtained without the addition of silver nitrate, indicating the presence of interfering materials. This precipitate was determined to be guanyl urea, equal to ammonia 0.21 per cent. Without extreme care in observation on the part of the analytical chemist in applying the Harger method this would have been reported as dicyanodiamide. After removal of the guanyl urea, silver nitrate was added and all the conditions of the Harger method followed out, and after adding the Harger correction factor dicyanodiamide equivalent to ammonia 0.03 per cent was obtained. A direct determination of urea showed urea equivalent to ammonia 0.66 per cent. Cyanamide equivalent to ammonia was determined as 0.06 and ammonia salts in terms of ammonia as 0.05 per cent. The above accounts for 1 per cent of ammonia out of a total of 1.2 per cent, the undetermined part being insoluble ammonia and forms which the writer could not determine analytically by accurate methods at his disposal.

This large-scale experiment, checked by two independent laboratories, seems to dispose effectually of the application of Harger's conclusions to even such an unusual kind of fertilizer mixture when prepared by actual manufacturers.

In order, however, to dispose of this matter finally, a considerable quantity of cyanamide was moistened and allowed to stand under such conditions as to insure about one-half of its nitrogen being converted into the dicyanodiamide form. The actual analysis of this cyanamide showed 10.8 per cent dicyanodiamide ammonia and approximately an equal quantity of cyanamide ammonia. A similar mixture with acid phosphate was made with this cyanamide which was positively known to contain dicyanodiamide, but strange to say the resulting mixture showed no test for the same upon analysis. In other words, the only conclusion is that dicyanodiamide is incapable of existence in such an acid mixture prepared according to the methods of the modern fertilizer mixing plant, all of which is quite in accord with the theory of its formation and decomposition.

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[1] Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published in revised form under the title of "The Changes Taking Place in Cyanamid when Mixed with Fertilizer Materials," THIS JOURNAL, **12** (1920), 1111.

[3] *Am. Fertilizer*, **54** (1921), 49; *Gaz. chim. ital.* (1918), II, No. 4, 358; *Trans. Am. Inst. Chem. Eng.*, **8** (1915) 267; Beilstein's "Handbuch der Organische Chemie."

[4] In the paper as printed the conclusion as above given was modified and changed in form.

[5] G. Grube and P. Nitsche, "The Polymerization of Cyanamide to Dicyanodiamide in Aqueous Solution," *Z. physik. Chem.*, **86**, 65 (1913); G. Grube, "Technical Methods for the Production of Dicyanodiamide from Lime Nitrogen from the Standpoint of Chemical Kinetics," *Z. angew. Chem.*, **27**, I, 368 (1914); D. R. P. 252,273; 279,133; 257,769.

Mixtures of Cyanamide with Base Goods

It has been known for a long time that amino acids react with cyanamide. In the few cases actually studied and reported in easily accessible literature,[6] the reaction products noted are excellent plant foods. A very large amount of work along the line of cyanamide reactions with amino acids has been published in the form of theses by German students, and a comprehensive review of these is being made at the present time in order to throw more light upon this phase of the behavior of cyanamide in fertilizer mixtures.

The use of rough ammoniates in base mixtures is quite common practice in this country. The resulting base goods contain the larger part of their available nitrogen in the form of amino acids, and a study has been made of the constitution of fertilizer mixtures made up by various factories from these bases with cyanamide and other ingredients. The results of a few of these studies follow.

A mixture was prepared in the proportions of 820 lbs. of a well-known base goods and 180 lbs. of cyanamide. To insure the most complete decomposition of the cyanamide, the material was allowed to stand for 30 days after mixing and before sampling for analysis. The result of the analysis, reported on the basis of the cyanamide ammonia added being taken as 100 per cent, was as follows:

	Per cent
Cyanamide ammonia	2.5
Dicyanodiamide ammonia	3.1
Urea ammonia	45.7
Ammonium salts	4.3

No part of the remainder of the cyanamide ammonia, amounting to 44.4 per cent, together with the ammonia in the ammoniated base could be positively identified in a quantitative way by any known method at our disposal. It undoubtedly represents complex amino-cyanamide derivatives for which we have no adequate analytical methods.

Two samples of ammoniated base goods, formulated 8–3–3 and 8–2–2 from two different fertilizer plants and representing material placed on the market in the fall of 1920 in large tonnage, were examined very carefully by the various analytical methods at our disposal. These fertilizers were each formulated with 70 lbs. of cyanamide to the ton of finished fertilizer and each also contained about 1400 lbs. of ammoniated base per ton. The 8–3–3 contained 13.8 per cent moisture and the 8–2–2 contained 12.87 per cent moisture, both samples having ample water to insure reaction like that reported by Harger. The other elements were tobacco stems, rapeseed mix, ammonium sulfate, potash, and filler. The samples were investigated several months after mixing and undoubtedly the chemical status had reached equilibrium. In neither of these samples was any dicyanodiamide or guanyl urea found, nor did they contain cyanamide. Both contained urea to the extent of 30 per cent for the 8–3–3, and 15 per cent for the 8–2–2 brand, of the equivalent of the cyanamide nitrogen added, but more than one-half of this cyanamide nitrogen could not be accounted for by any of the analytical methods at our disposal.

In view of the fact that we were looking for dicyanodiamide in these materials and were somewhat fearful that the various methods might fail to show its presence, we added 50 mg. of pure dicyanodiamide to water extracts of 8 g. of the 8–3–3 fertilizer mixture and proceeded with a determination by the Harger method. In two experiments carried out as nearly in duplicate as possible, only 39 mg. of dicyanodiamide in one case were recovered and 14.1 mg. in the other. In a third experiment where 35 mg. of dicyanodiamide were added to the water extract from 4 g. of the fertilizer, no precipitate whatever was obtained.

In view of this peculiar behavior of the 8–3–3 fertilizer, the 8–2–2 fertilizer, which was very similar in constitution, was not tested similarly at the time. Instead, a sample was obtained of a 7–7–5 brand, formulated with 820 lbs. of ammoniated base, 300 lbs. of 16 per cent acid phosphate, and 80 lbs. of cyanamide, together with 800 lbs. of tobacco stems, meal, ammonium sulfate, and muriate of potash. The moisture content of this fertilizer, which was marketed in large quantities last winter, was 9.94 per cent. No test for dicyanodiamide was obtained by any of the various methods, and dicyanodiamide was added to the sample, which was then analyzed by the Harger method. Four aqueous extracts were prepared on four samples of 4 g. each of the fertilizer, the use of the smaller samples of the fertilizer seemingly giving more accurate check results. To one of these samples 25 mg. dicyanodiamide were added, to the second 50 mg., to the third 75 mg., and one to the fourth 100 mg. In each case practically all the dicyanodiamide added was recovered by the Harger method. Of the total of 250 mg. of dicyanodiamide added in the four lots, a total of 253.2 mg. was obtained. If we assume this extra 3.2 mg. of dicyanodiamide recovered to represent the dicyanodiamide content of 16 g. of fertilizer treated, this product would have contained a total of 0.02 per cent dicyanodiamide expressed in terms of ammonia. This was the only fertilizer mixture containing ammoniated base in which the present investigators ever succeeded in recovering quantities of dicyanodiamide comparable to that added.

Feeling that possibly the tobacco stems and meals might have had some influence on the application of the Harger method to the determination of dicyanodiamide in these mixtures, we procured some samples of standard base goods from some of the large producers. One of the samples contained 2.56 per cent of ammonia, of which 75 per cent was water-soluble, and of which about 25 per cent was yielded as ammonia on distillation with magnesia. Several 10-g. portions of this ammoniated base were extracted with water and treated by the Harger method up to the point of addition of picric acid. Four portions were prepared, each corresponding to 4 g. of ammoniated base. To the first portion 20 mg. of dicyanodiamide were added, to the second portion 40 mg., to the third portion 60 mg., and to the fourth portion 80 mg. The picric acid addition and the ice bath treatment were then carried out. The portion containing 80 mg. of dicyanodiamide began to precipitate in 15 min., and the portion containing 60 mg. at the end of 25 min. No precipitates were obtained from the other portions, even at the end of an hour. All four samples were allowed to stand over night, those to which the 20 and 40 mg. additions of dicyanodiamide showing no precipitate on this long standing. From the portion to which the 80 mg. of dicyanodiamide had been added, only 54 mg. were recovered and from the portion containing 60 mg. of dicyanodiamide only 37 mg. were recovered. These experiments confirm our theories that the amino acids of the base mixture not only react with cyanamide, as is well known, but also have the property of reacting with dicyanodiamide to a certain extent, and that it would be impossible to have dicyanodiamide in a fertilizer mixture containing base goods and cyanamide when the latter is used in the recommended proportions.

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[6] Richter, 3rd American Edition, 412; *Ber.*, **43** (1910), 2882, *Gaz. chim. ital.*, **45** (1915), 56.

In a parallel series of experiments to which cyanamide had been added, it was found that 4 g. of ammoniated base had the property of reacting immediately with approximately 15 mg. of cyanamide. Ordinarily this reaction between cyanamide and the base goods seems extremely rapid, but it was later found that the rapidity of this reaction was affected by the quantity of ammonium salts present in the aqueous extract of the base goods. The complex nature of this reaction on cyanamide prevented our obtaining any precise information which would enable us to plot the rate of this reaction with cyanamide. Certain complex guanidines, which could not be isolated and identified specifically, seemed to be formed in the presence of the ammonium salts.

CONCLUSION

From these few experimental results with samples of commercial fertilizer and special mixtures from various plants and various agricultural chemical companies, subjected to all the available analytical methods that offer any possibilities of yielding accurate results, the present writer has been entirely unable to parallel the conclusions enunciated in the Harger paper. Wherever dicyanodiamide has been found it has been in extremely small quantity, hardly exceeding the limit of precision of the method of analysis available. Every possible endeavor has been made to check the methods, prove them for their application to the case in question, or to confirm results by the use of several methods of analysis. The widest possible ranges of fertilizer mixtures have been studied. Straight mixtures of ammoniated base and cyanamide are at the present time undergoing extensive investigation with the idea of learning more of the various forms of cyanamide decomposition products therein and applying this information to the commercial fertilizer mixtures. While this work is far from complete, we have in no case encountered dicyanodiamide in even these simple mixtures. The recovery of direct dicyanodiamide additions has yielded extremely irregular results. For this irregularity we have no adequate explanation in many cases.

Methods are lacking for the constitutional analysis of these complex nitrogen compounds. Our own laboratory has been at work on these methods for years. We have reached only to the stage where we are absolutely certain of determinations of ammonium salts, cyanamide, guanyl urea, and urea.

In the case of dicyanodiamide ammonia, we are certain of the results in the absence of amino acids and other organic materials. In the majority of such cases we can check our results by transformation of the dicyanodiamide to guanyl urea and its determination as such. In the presence of amino acids we are able to prove accuracy of results in most cases, but we have records of a few examples where we cannot prove definitely whether the methods of analysis are applicable or not. In several cases we have encountered difficulties with some of the proposed methods because decomposition takes place incident to the reagents used or conditions imposed in the carrying out of the method. This has been a source of considerable difficulty which we believe has been overlooked by many of the investigators in this field who have not familiarized themselves with the character of cyanamide decompositions.

Our conclusion to-day is that in the ordinary commercial fertilizer formulated from the everyday fertilizer materials, and using cyanamide in the quantities recommended, there need be no fear of transformation to dicyanodiamide and consequent loss of the plant food value of the nitrogen contained.

The complex fertilizer mixtures of to-day, and particularly those containing cyanamide, form a most attractive field for investigation of their constitution, and should be of great interest to the student of analytical chemistry desirous of investigating one of the most complicated, yet fascinating fields of his activity. The ability to determine the various forms of nitrogen in such a fertilizer mixture is very greatly desired and chemists have been coöperating and working on these methods in several laboratories for a considerable period of time; yet the field to-day is practically untouched.

Comments on Formation of Dicyanodiamide in Fertilizers[1]

By J. E. Breckenridge

American Agricultural Chemical Co., Carteret, New Jersey

In experiments made by R. N. Harger,[2] mixtures were made to correspond to 25, 50, 75, and 100 lbs. of cyanamide per ton of fertilizer with water added so that mixture contained 10 per cent moisture. Harger writes, "It will be noticed that while the formation of dicyanodiamide is less with smaller quantities of cyanamide used in the fertilizer, yet the change to dicyanodiamide is still very considerable with 50 pounds per ton."

In view of the fact that cyanamide had been used for some years in amounts approximating 50 lbs. to the ton, this statement disturbed the fertilizer industry, and there was some doubt as to whether or not in actual fertilizer manufacture there would be the results as indicated by the above experiments. No harmful results had been called to the writer's attention by the use of cyanamide as used in mixed fertilizers.

The author, therefore, prepared a laboratory mixture of 1900 parts acid phosphate (testing 12 per cent moisture and 16.50 per cent available phosphoric acid) and 100 parts of cyanamide (old stock). This mixture was tested at once for dicyanodiamide by the method outlined by Harger, with the following results:

	Dicyanodiamide Per cent
Fresh mixture	0.15
24 hours	0.26
9 days	None

Again a pile of fertilizer in the factory was sampled. This contained 40 lbs. of cyanamide to the ton, the other ingredients being the usual materials entering a fertilizer mixture, with 8 per cent phosphoric acid. The fertilizer was acid in reaction and was made up as in regular manufacture, in several hundred tons to a pile. This sample was tested for dicyanodiamide, and none was found.

The sample was sent to the Bureau of Plant Industry (Soil Fertility Investigations), Washington, D. C., and under date of September 28, 1920, the reply was "The examination of this sample of fertilizer in the Laboratory here shows it to be practically free from dicyanodiamide."

Since that proportion of cyanamide in the sample submitted was about what is used in fertilizer manufacture, the result confirmed our experience in the past; namely, that in general fertilizer manufacture no dicyanodiamide is present in fertilizers as shipped to the trade when 40 lbs. of cyanamide are used in complete goods containing 8 per cent available phosphoric acid, and that the conclusion reached by Harger is not confirmed in general fertilizer manufacture.

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[1] Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] This Journal, **12** (1920), 1111.

Electrolytic Recovery of Magnesium from Salt Works Residue[1]

By K. S. Boynton and Verne Langford with J. F. G. Hicks

Department of Chemistry, Stanford University, Stanford, California

In view of the fact that the raw materials and power necessary for the production of magnesium at a comparatively low cost are to be found on the Pacific Coast, the problem of producing the metal from these raw materials was undertaken.

Raw Materials

In the experimental work crude hydrated magnesium chloride, commonly called "bittern," was used as the source of magnesium. Large quantities of this bittern form the residues from the recovery of salt from sea water. The composition is as follows:

	Per cent
Insoluble	0.05
Ferric and aluminium chlorides	Trace
Calcium chloride	0.59
$MgCl_2.6H_2O$	94.42
Sodium and potassium chlorides	4.32
$MgSO_4.7H_2O$	0.59

Commercial ammonium chloride and sodium chloride were used as dehydrating agents. Dehydration of the magnesium chloride by heating it alone always resulted in the formation of basic salts, and the dehydrated mass was worthless for electrolytic purposes. The mixture finally selected contained:

	Parts
$MgCl_2.6H_2O$	10.0
NaCl	1.
NH_4Cl	1.0

The following advantages are claimed for it:

1—Reduction of hydrolysis to a minimum.
2—Minimum amounts of sodium and ammonium chlorides.
3—A maximum current efficiency.
4—A maximum concentration of magnesium in the bath, for electrolysis
5—Lowest viscosity of any bath tried.
6—Higher percentage yield.
7—Relatively low melting point.

Dehydration of Crude Magnesium Chloride

This mixture was dehydrated by heating gradually to 200° C. in a revolving steel cylinder, through which air was forced for the more rapid removal of steam and small quantities of hydrochloric acid gas. A few flint pebbles in the cylinder served to keep the mixture broken up. The anhydrous chlorides were heated in iron pots until ammonium chloride was entirely driven off, and the residue had melted. This fusion was electrolyzed.

Electrolysis

Two types of electrolytic cell were used: In one, both electrodes were carbon; in the other, the anode was carbon and the cathode iron. Two patterns of the carbon-iron cell, one the ordinary cylindrical pattern, and the other V-shaped, were found to be satisfactory. The carbon-carbon cell yielded the best results from a laboratory standpoint, but was considered impractical for work on a large scale.

Electrolyses were conducted in an atmosphere of illuminating gas. Obviously, any other cheap reducing or neutral atmosphere would answer the same purpose. It was possible to produce metal at a minimum voltage of 4, but the average for eleven runs was 6.2. As only a small generator was available for these experimental runs, the average amperage was only 100.

The average faraday efficiency for eleven runs with the iron cylindrical cell was 30 per cent, and the average time was 1.7 hrs. After readily reproducible conditions were obtained, it was a comparatively simple matter to predict the yield of a given run to within 25 per cent of the actual yield.

Purification of the Magnesium

Metallic magnesium was deposited at the cathode surface in small molten globules or "shot," which slowly increased in size and were finally detached by the convection currents set up in the bath. These currents distributed the globules throughout the bath, the specific gravity of which was very nearly that of the globules. This accounts for the fact that the globules could be skimmed from the surface of the bath or scraped from the bottom of the cell during the same run.

At the end of each run the fusion was poured into a mold, cooled and crushed, and the metal was sieved out. The "buttons" of magnesium varied in size from minute spheres to globules weighing over half a gram.

To free the metal from occluded flux, carbon particles, oxides, etc., some dehydrated magnesium chloride was fused in a carbon crucible, fitted with an air-tight lid containing two holes to permit ingress and egress of illuminating gas. The magnesium shot were thrown into the fused mass and the lid clamped on tightly. The degree of purification of the metal is shown by the following table:

	Crude Magnesium Per cent	Refined Magnesium Per cent
Insoluble	Trace	None
Iron	0.74	0.42
Aluminium	Trace	Trace
Calcium	Trace	Trace
MgO	0.02	Trace
Magnesium	99.24	99.58

Recovery of Volatilized Ammonium Chloride

Some experiments were made on the possibility of recovering the ammonium chloride by condensation. Small amounts of moisture very markedly lowered the efficiency of this condensation process, although better than 50 per cent recoveries were easily attained.

Estimate of Cost of Producing Magnesium on San Francisco Bay

From the analysis of crude "bittern" it will be seen that, theoretically, 8.88 tons (2000 lbs.) of this raw material are required to produce 1 ton of magnesium. Allowing 25 per cent wastage to maintain the purity of the electrolyte, 11.10 tons of "bittern," 1.64 tons of salt, and 1.11 tons of ammonium chloride will be required to produce a ton of metal.

DEHYDRATION—Since hydrated magnesium chloride contains 53.5 per cent of water, the weight of water in 11.10 tons of raw material would be 5.94 tons. One barrel of fuel oil will evaporate 1.3 tons of water in dehydrating alum. As the "bittern" loses its water at a lower temperature than alum, the above ratio seems to be a safe estimate. At this rate 4.57 bbls., or, to allow 10 per cent for removal of additional moisture of the mixture, 5.02 bbls. of fuel oil would be required for the dehydration of sufficient material to produce one ton of magnesium.

TIME AND POWER NECESSARY TO DEPOSIT ONE TON OF MAGNESIUM AT A FARADAY EFFICIENCY OF 30 PER CENT—1 faraday = 96, 500 coulombs = 0.0264 lb. of magnesium. $\frac{2000}{0.0264}$ = 75,757.57 faradays = 7,310,605,505 coulombs per ton of magnesium.

Therefore, to produce 1 ton of magnesium 24,368,685,010 coulombs would be needed.

$$\frac{24{,}368{,}685.010}{3600} = 6{,}769{,}079 \text{ ampere hours to produce a ton}$$

$$\frac{6759}{720 \text{ (hrs. in 1 mo.)}} = 9401.4 \text{ ampere months}$$

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[1] Received August 18, 1921.

$$9401.4 \times 6 \text{ (volts)} = 56.41 \text{ kw.-mo.}$$

Allowing 25 per cent (14.10) for interruptions, 70.51 kw.-mo. would be required for the production of 2000 lbs.

FREIGHT AND HANDLING OF RAW MATERIALS—The plant would be within a few miles of the source of the raw material, hence freight and handling would be a comparatively small item of expense. For each ton of metal produced, 18.85 tons of material would need to be freighted and handled.

LABOR—Six men, including a chemist, would handle the proposed plant.

OIL FOR HEATING CELL—The crude oil for outside heating of the cell would be required, at most, during one-fourth of the run. For this heating 5 tons would be required.

CARBON ANODES—About 200 lbs. of carbon anodes would be consumed per ton of metal.

ILLUMINATING GAS—For a cell of sufficient size to produce a ton of magnesium in 720 hrs., 50,000 cu. ft. of illuminating gas would be required to form a reducing atmosphere above the electrolyte.

COST OF PRODUCING 1 TON OF MAGNESIUM

Crude $MgCl_2.6H_2O$	11.1 tons at $30.00	$ 333.00
Commercial NH_4Cl	11.1 tons at $60.30	67.00
Commercial NaCl	1.64 tons at $7.00	11.48
Oil for dehydration	5.02 bbls. at $1.80	9.04
Illuminating gas	50,000 cu. ft. at $0.50	25.00
Electric power	70.51 kw.-mo. at $4.00..........	282.04
Oil for heating cell	5 tons at $10.00	50.00
Anode carbon	200 lbs. at $0.04	8.00
Freight and handling of raw materials	18.85 tons at $5.00	94.25
Labor	6 men, including a chemist	1000.00
	TOTAL..............	$1879.81

$$\frac{1879.81}{2000} = \$0.939 \text{ per lb. to produce a ton of magnesium}$$

Loss of Carbon Dioxide from Dough as an Index of Flour Strength[1,2]

By C. H. Bailey and Mildred Weigley

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Flour strength studies conducted during the past quarter century have usually employed as the ultimate criterion of strength the comparative physical properties of yeast-leavened loaves of bread produced on baking. Humphries and Biffin[3] suggest that "a strong wheat is one which yields flour capable of making large, well-piled loaves." Quality of the loaves is thus determined by their size or volume, and the texture and other related properties of the crumb. Baking tests, however, are not exact procedures which yield uniform results when the same materials are employed. Judgment comes into play to a considerable extent, and experts sometimes differ in their opinion of the relative merits of different flours which are being compared. Such tests do not of necessity indicate the reasons for variations that are observed, or the methods for effecting desired improvements. For these reasons efforts have been directed toward developing more exact methods for testing the properties of flour that are of significance in this connection. The work reported in this paper represents an attempt in this general direction.

PROPERTIES THAT CONSTITUTE STRENGTH

A consideration of the factors involved in the production of "large well-piled" loaves suggested to one of the authors[4] that "the strength of flour is determined by the ratio between the rate of production of carbon dioxide in and the rate of loss of carbon dioxide from, the fermenting mass of dough." The absolute rate of carbon dioxide production in doughs made from different flours varies, to be sure, through fairly wide limits. When known, the rate can be varied in the desired direction, however, by adjustments in the formula, and particularly in the proportions of yeast, yeast accelerators, salt, fermentable sugars, and diastase preparations. The retention of gas is much more difficult to bring under control, since it is apparently determined in large measure by the percentage and physical properties of the gluten proteins in the flour. Hence, in testing flours, the ratio between production and loss of carbon dioxide apparently becomes of practical significance, and this was the point attacked in the present investigation.

CHARACTER OF FLOURS EMPLOYED IN INVESTIGATION

Two flours were employed, a "strong" flour milled from hard spring wheat, and a "weak" flour milled at Spokane, Washington, from typical soft wheat of that region. The composition, and the baking qualities of the two flours, determined by the method previously described by Bailey,[4] are shown in Table I. The strong flour contained a materially higher percentage of crude protein, and on baking gave a loaf of larger volume and better texture than did the weak flour. The differences in these respects were considerable. As the flours were of about the same grade, as indicated by the ash content and color score, they were well suited to a study of properties responsible for variations in baking strength.

TABLE I—ANALYSES AND BAKING TESTS OF STRONG AND WEAK FLOURS

MARK	Moisture Per cent	Crude Protein (N × 5.7) Per cent	Ash Per cent	Volume of Loaf Cc.	Color Score	Texture	Expansimeter Test Cc.
B878, weak flour......	10.88	8.00	0.52	1200	97	85	520
Composite, strong flour	8.95	12.00	0.56	1580	98	100	910

That the two flours also varied widely in colloidal properties was established by the procedure developed by Gortner and Sharp,[5] in which the change in viscosity of a mixture of water and on the addition of normal lactic acid solution is traced by a MacMichael viscosimeter. Table II gives the results of this test.[6] Quite evidently there are decided differences in the properties of these two flours which are responsible for variations in the viscosity of such preparations. The

TABLE II—VISCOSITY IN MACMICHAEL DEGREES OF FLOUR AND WATER MIXTURES OF WEAK AND STRONG FLOURS

(Mixture contained equivalent of 25 g. dry matter + 100 cc. water)

Normal Lactic Acid Added Cc.	Weak Flour (B878) Degrees MacMichael	Strong Flour (Composite) Degrees MacMichael
0.0	32	68
0.5	32	73
1.0	38	104
1.5	43	135
2.0	50	161
2.5	53	183
3.0	56	196
4.0	60	212
5.0	61	221
6.0	62	222
8.0	62	222
10.0	61	219

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[1] Presented before the Division of Biological Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published with the approval of the Director as Paper No. 274, Journal Series, Minnesota Agricultural Experiment Station.

[3] "The Improvement of English Wheat," *J. Agr. Sci.*, **2** (1907), 1.

[4] C. H. Bailey, THIS JOURNAL, **8** (1916), 208.

[5] "The Physicochemical Properties of Strong and Weak Flours. III—Viscosity as a Measure of Hydration Capacity and the Relation of the Hydrogen-Ion Concentration to Imbibition in the Different Acids." Presented before the Division of Physical and Inorganic Chemistry at the 62nd Meeting, A. C. S., New York, N. Y., September 6 to 10, 1921.

[6] Determinations made by Paul F. Sharp.

flour which is regarded as "strong" on the basis of the baking tests gives a much more viscous preparation when mixed with water and lactic acid than does the weak flour.

Method of Determining Loss of Carbon Dioxide from Dough

The two flours were mixed into doughs with a mechanical dough mixer, using the following formula:

	Grams
Flour	350.0
Yeast	4.25
Salt	5.25
Sugar	8.75
Water	Sufficient

The water used in preparing the weak flour dough was equivalent to an average of 56 cc. per 100 g. of flour, while with the strong flour an average of 61.4 cc. per 100 g. of flour was used. These proportions of water resulted in doughs of as nearly the same consistency as could be produced with flours of such different properties.

Two series of determinations were made with these doughs. In the first, the dough was divided into aliquot parts, and the determination of the diffusion of carbon dioxide out of the dough was begun without any preliminary fermentation. Such doughs are referred to in the following discussion as "no previous fermentation" doughs. After removal from the mixer, the other series of doughs were allowed to ferment for several hours in a thermostat at 28° C. before the diffusion of carbon dioxide was determined. These doughs are designated as "normally fermented." The fermentation period varied somewhat, averaging 274 min. in the case of the strong flour and 248 min. in the case of the weak flour. During this period the doughs were "punched" or worked lightly three times. At the end of the period the doughs were regarded as ready for molding into loaves, and were accordingly kneaded vigorously on the bread board to remove as much as possible of the occluded gas.

In both series the doughs were weighed, and three aliquot portions were scaled off, each representing one-seventh of the total dough, or 50 g. of flour. All three portions were subjected to the same treatment with respect to kneading and molding. The first was dropped into a 1000-cc. measuring cylinder which contained 600 cc. of water and its volume was determined by the rise in the water level. The second portion was molded into a cylindrical form and placed in a dry 250-cc. measuring cylinder where its subsequent volume could be determined as fermentation proceeded. The third portion was molded to fit a shallow iron pan, about 7 cm. in diameter and 1.8 cm. deep. This quantity of dough filled the round pan about level full when firmed down. The pan was covered with a ground glass plate in an inverted dialyzer. The plate and the neck of the dialyzer were fitted with tubes as shown in Fig. 1. Both tubes were tightly sealed in place with wax and, when the glass plate was vaselined and seated, constituted the only means for the passage of gases into and out of the apparatus. The entire apparatus was placed in an air thermostat maintained at 34° C. (93.2° F.).

The inlet tube in the plate was connected to a source of moist, CO_2-free air at 34° C. (This air had been bubbled through 50 per cent sodium hydroxide solution, and then through water into a large cylinder where it attained the temperature of the thermostat before entering the dialyzer or fermentation chamber.) The outlet tube was connected to a Truog[7] tower as modified by Bailey,[8] where the carbon dioxide was absorbed in a known amount of barium hydroxide solution. The residual barium hydroxide was determined at the end of the absorption period by titration with standard hydrochloric acid solution. The titration data were calculated over into terms of milligrams of carbon dioxide.

It was customary in these experiments to collect the gas given off during a period of exactly 30 min., then to switch the outlet tube to another Truog tower, where the gas was collected for another 30-min. period. During the second period it was possible to determine the residual barium hydroxide in the first tower, and recharge it for the third 30-min. period. In this way two towers served for the determination by 30-min. periods of the gas diffusing out of each dough until it definitely "fell" or partly collapsed. At the end of each period the volume of the dough in the graduated cylinder was noted, and these values, minus the initial volume of the same dough, represented the *increase* in volume due to retention or occlusion of the gases of fermentation. The maximum volume attained by each dough was recorded.

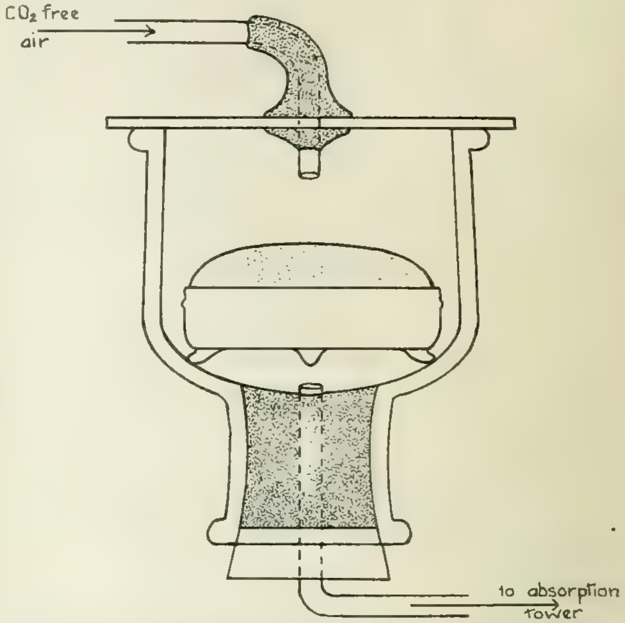

Fig. 1—Chamber and Dough Arranged for Determination of Loss of Carbon Dioxide during Fermentation

Relation of Strength to Gas Retention

Table III and Figs. 2 and 3 give the average data obtained with the strong and weak flours. From five to nine replicates are included in each set of averages in the table. Two series of comparisons are thus afforded: (*a*) The loss of carbon dioxide from the doughs per unit of time, and (*b*) the expansion of the dough per unit of time. The graphs establish the fact that the weak flour dough consistently lost more carbon dioxide per unit of time than did the strong flour dough. The largest relative difference is found at the end of 120 min. in the doughs not previously fermented when the strong flour dough had lost a total of only 56.6 mg. of carbon dioxide in expanding 140 cc., while the weak flour dough had lost a total of 113.0 mg. of carbon dioxide in expanding 120 cc. Less difference in the loss of carbon dioxide per unit of time was found when the strong and weak flour doughs fermented normally were compared. Such differences as existed were uniformly in the direction of smaller losses from the strong flour dough. The total losses of carbon dioxide up to the time of falling or collapse of the two doughs were apparently about the same in both cases, but owing to the difficulty in judging of the exact time when such a collapse or fall occurred, it was impossible to determine with precision the total loss of gas up to that time. The general shape of the curves, the distance between them, and the quantity of gas lost up to the point where the curves begin to "break" or change shape sharply appear of more significance than the quantity of gas lost up to the time of apparent collapse of the dough.

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[7] This Journal, **7** (1915), 1045.

[8] "Respiration of Shelled Corn," Minnesota Agricultural Experiment Station, *Technical Bulletin* **3**.

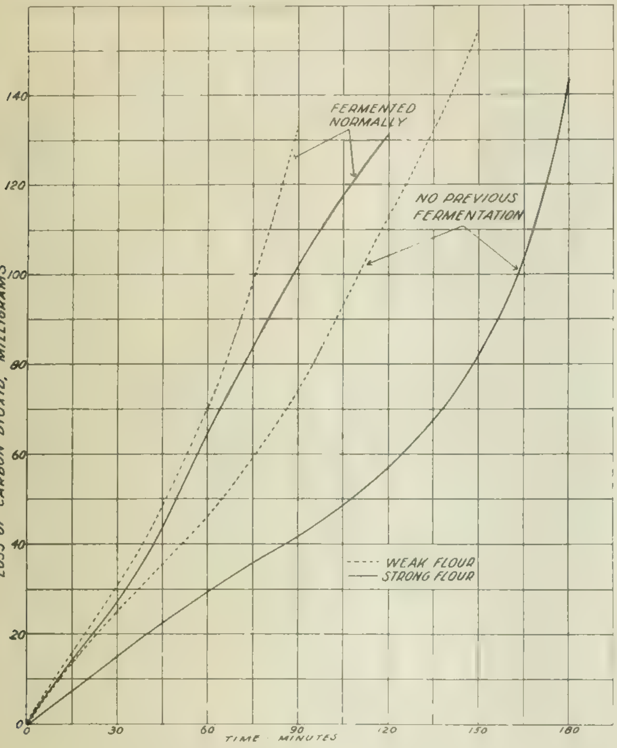

Fig. 2—Loss of Carbon Dioxide from Dough per Unit of Time

The rate of expansion of the strong flour dough was considerably greater than that of the weak flour dough. This is usual in such instances when an adequate quantity of sugar is included in the formula. In the case of each flour, the normally fermented doughs exhibited greater differences than the doughs not previously fermented. This was due to the fact that both of the weak flour doughs expanded to about the same maximum volume, while the strong flour normally fermented dough expanded considerably more than the strong flour dough not previously fermented.

Table III—Average Loss of Carbon Dioxide from, and Change in Volume of, Doughs Made from Strong and Weak Flours

Strong Flour				Weak Flour			
Time Min.	Total Carbon Dioxide Loss Mg.	Total Volume of Dough Cc.	Increase in Volume of Dough Cc.	Time Min.	Total Carbon Dioxide Loss Mg.	Total Volume of Dough Cc.	Increase in Volume of Dough Cc.
			No previous fermentation				
0	...	63	0	0	...	63	0
30	15.1	78	15	30	25.4	74	9
60	29.6	113	50	60	46.3	101	38
90	41.9	165	102	90	74.0	144	81
120	56.6	203	140	120	113.0	183	120
150	81.8	226	163	150	154.7	192	129
180	143.9	226	163	...	...	...	...
			Fermented normally				
0	...	71	0	0	...	62	0
30	27.4	145	74	30	31.0	128	46
60	64.9	219	148	60	71.0	176	114
90	101.6	254	183	90	133.5	189	127
120	131.4	266	195	...	...	...	...

The data presented in Figs. 2 and 3 are combined in Fig. 4 and the losses of carbon dioxide are plotted against the change in volume of the corresponding dough. These data appear to be the most significant in this connection and establish considerable differences in the properties of the strong and weak flour doughs. It is evident that the weak flour dough lost decidedly more carbon dioxide per unit increase in volume from the start, and that when the dough began to collapse and break down it discharged carbon dioxide into the surrounding atmosphere at a much greater rate than did the strong flour dough. Thus when the normally fermented strong and weak flour doughs had expanded 80 cc. they had lost 30 and 42 mg. of carbon dioxide, respectively, and when they had expanded 120 cc. they had lost 50 and 100 mg. Even greater differences between the two flours are observed when the doughs not previously fermented are compared.

Changes in Expansion and Gas Retention of Dough as Result of Fermentation

Fig. 3 affords an interesting comparison of the strong and weak flour doughs as affected by previous fermentation. Both weak flour doughs expanded to the same extent, while corresponding strong flour doughs expanded 163 cc. when not previously fermented and 195 cc. when fermented normally. This suggests that fermentation effects more improvement in the properties of a strong flour dough than is brought about by a similar treatment of a weak flour dough.

The maximum volumes attained by the strong and weak flour doughs fermented normally differ in the usual direction. The curve representing expansion of the weak flour dough rises less rapidly and breaks earlier and more sharply than the corresponding curve for the strong flour dough. Instances have been occasionally observed in this laboratory where such a relation did not exist. For example, in comparing certain clear grade flours with the patent grade from the same mill, the clear grade dough would sometimes expand more rapidly and to a slightly greater maximum, although other aliquot portions of the same doughs when baked gave larger, better-textured loaves from the patent flour dough. For this reason some doubt has been cast upon the accuracy of a simple expansion test as an index of baking quality. Such data, considered in connection with the losses of carbon dioxide,

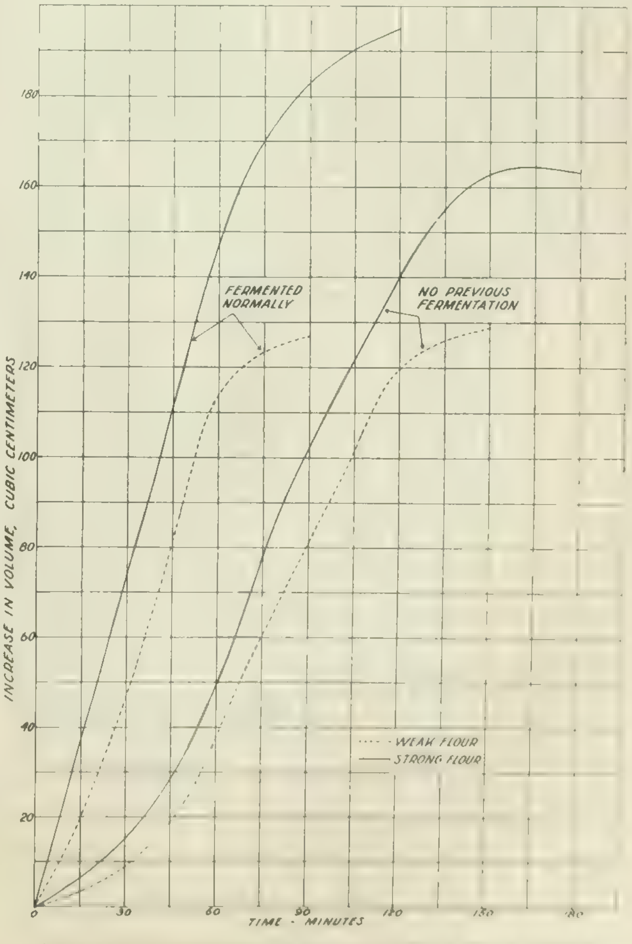

Fig. 3—Rate of Expansion of Strong and Weak Flour Doughs

are of service in indicating the rate of gas production in the dough, which is one of the significant factors in determining baking strength.

The curves also indicate a decided difference in the rate of expansion of the doughs immediately after mixing (no previous fermentation) and similar doughs after normally fermenting for several hours. The former expanded slowly during the first hour, more rapidly during the second hour, and continued to expand somewhat during part or all of the third hour. Doughs normally fermented, on the other hand, expanded more rapidly during the initial period, and exhibited a diminishing rate during each successive period. They always reached their maximum volume sooner than the doughs not previously fermented which were made with the same flour, and tended to collapse or fall more suddenly.

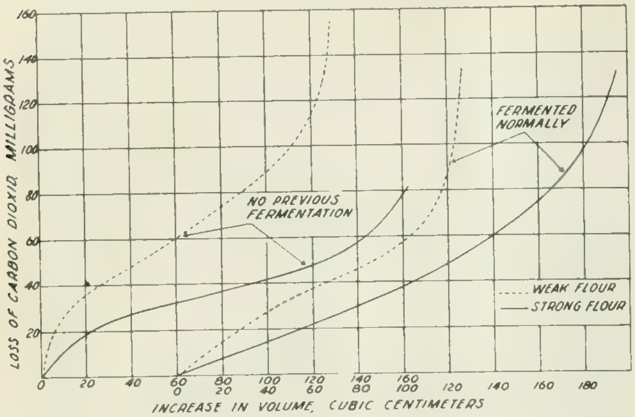

Fig. 4—Relation of Expansion of Strong and Weak Flour Doughs to Loss of Carbon Dioxide

The relatively slow expansion of the doughs not previously fermented cannot be attributed to excessive loss of carbon dioxide during this time, for reference to Fig. 3 establishes the fact that they actually lost less carbon dioxide per unit of time than the normally fermented doughs. It is not likely that the fermentation rate, and consequently the quantity of carbon dioxide produced in the dough, is reduced in any such proportion as is observed in the expansion of these doughs. This suggests that a part of the carbon dioxide produced at the outset becomes "dissolved" in the dough without effecting an appreciable expansion of the mass. In fact, it may be that "ripening" of the dough and its readiness for molding into loaves is in part related to the progressive solution of carbon dioxide in the dough during fermentation. Such dissolved carbon dioxide would constitute a reservoir of gas largely available for effecting the expansion or spring of dough when placed in the oven for baking, since it would tend to distil into the vesicles already present in the interior of the mass and to extend or enlarge their volume. So far as we are aware, there are no published data relating to the proportion of free or gaseous carbon dioxide in the vesicles and of dissolved carbon dioxide in the dough, and it appears desirable to study the fermentation of bread doughs from that angle to ascertain (*a*) whether such a progressive solution of carbon dioxide in the dough occurs and (*b*) whether significant variations exist in the quantity of carbon dioxide dissolved in different doughs.

After the dough has fermented several hours and is ready to be molded into loaves, it is probably saturated with carbon dioxide. All the carbon dioxide subsequently produced will be occluded and serve to expand the mass, or will diffuse or be discharged into the atmosphere. Assuming that the expansion of fermented doughs is accomplished by the occlusion of carbon dioxide resulting from fermentation and assuming further that such carbon dioxide is under atmospheric pressure of about 730 mm. in the dough at a temperature of about 30° C., it follows that each milligram of carbon dioxide will expand the dough 0.59 cc. Thus each cubic centimeter of increased volume will represent at least 1.7 mg. of carbon dioxide. The normally fermented strong flour dough in expanding 120 cc. thus occluded at least 204 mg. of carbon dioxide and lost about 40 mg. The ratio of gas lost to total gas produced was thus about 40 : 244, or approximately 1 : 6. The corresponding weak flour dough, in occluding 204 mg. of carbon dioxide and expanding 120 cc., lost about 100 mg. of carbon dioxide, a ratio of 100 : 304 or about 2 : 6. While these ratios are not precise because they are based on certain assumptions, they appear to be of service in establishing significant differences in the properties of such flours.

SUMMARY

Strength of flour is apparently determined by the factors which control the rate of carbon dioxide production in, and loss of carbon dioxide from, fermenting dough. The loss of carbon dioxide per unit increase in volume under controlled conditions affords a useful measure of the gas-holding capacity of dough. A procedure is described by means of which such data may be obtained for comparing different flours.

It is further suggested that "ripening" of dough during fermentation may be in part the result of solution in the dough of carbon dioxide, which may later become available for expanding the loaf when the latter is placed in the oven to bake.

Report of American Committee on Electrolysis

The American Committee on Electrolysis, which is made up of representatives of the large national associations of public utility corporations and of the Bureau of Standards, has recently issued its second report. The report includes discussions of design, construction, operation and maintenance of underground structures affected by electrolysis, as well as discussions of electrolysis surveys and apparatus for electrolysis testing. It concludes with an analysis of present European practice relating to electrolysis mitigation, and an outline of researches which the committee consider necessary in this connection.

This report is for sale by the American Institute of Electrical Engineers, 33 West 39th St., New York City, at one dollar per copy.

The United States Civil Service Commission has announced examinations for chemical technologist at $3600 to $5000 a year, associate chemical technologist at $2500 to $3600 a year, and assistant chemical technologist at $1800 to $2500 a year to fill vacancies in the Chemical Warfare Service, Edgewood Arsenal, Md. Applicants must qualify in at least one of the following branches of chemistry: advanced inorganic, analytical, biological, explosives, metallurgical, organic, pharmaceutical, physical, and engineering. Applications must be filed before February 14.

Examinations have also been announced for assistant examiner, Patent Office, at $1500 a year, to take place February 8, 9, and 10 and March 22, 23, and 24. Competitors will be rated on the following subjects: mathematics, physics, mechanical drawings, language, technics, and optional subject chosen from one of the following: mechanical engineering, civil engineering, electrical engineering, general chemistry, electrochemistry, and chemical engineering.

A short course in pulp and paper manufacture is to be given next year at the New York State College of Forestry at Syracuse University. The course will include elementary chemistry, elementary forestry, principles of pulp and paper manufacture, pulp and paper mill machinery, manufacture and testing of pulp and paper mill chemicals, manufacture of pulp and paper, practical paper testing, identification of woods and fibers, lectures, talks, and round-table discussion by prominent men in the industry, and inspection trips to a number of the larger mills and mill equipment manufacturers of New York State.

ADDRESSES AND CONTRIBUTED ARTICLES

Possibilities of the Plant Growth of the Moist Tropics to Furnish Materials for Liquid Fuel[1]

[ABSTRACT]

By H. N. Whitford

Yale School of Forestry, Yale University, New Haven, Connecticut

The future scarcity of the country's liquid fuel supply is now so apparent that the question of its early replacement has become a vital problem in natural economics. A question involving the annual synthesis of some 4,900,000,000 gallons of a feasible gasoline substitute calls for the development of new ideas and new sources of energy. Our one great source of energy is undoubtedly that of the sun. How can this source best be utilized? Obviously in the growth of plant life from which, in turn, alcohol and other fuels may be made.

The present paper is intended to consider the possibilities of the tropics as a source of transformed solar energy capable of being utilized for the production of liquid fuel.

FOREST CROPS

WOOD CROPS—The raw material which is most abundant as a product of the energy of the sun is wood and the moist regions of all tropical countries still contain vast areas covered with virgin forests. Only in the moist tropics is growth so rapid that enormous crops of wood could be raised in short time, in order that quantities of wood sufficient to supply a large alcohol-producing plant could be raised on a small area. In temperate regions nature's cellulose-producing factory is working only part time; in the moist tropics, because of continuous heat and available moisture, it is running full time. Besides, the energy of the tropical sun is greater. Theoretically the moist tropics should have two or more times the capacity to produce a given quantity of cellulose in a given time than temperate regions. Practically such is the case. Measurements of certain species of soft hardwoods in the tropics indicate that they grow from three to five times as rapidly as such woods as cottonwood and white birch in our climates. One acre of ground in the tropics can be made to yield as much timber in a given time as five or more acres in temperate regions, and, other things being equal, the cost of assembling this raw material at the factory would be greatly reduced.

BAMBOO CROPS—Measurements made in the Philippines show that culms of certain species of bamboo will attain a height of from 66 to 82 feet in a single season; most of the growth takes place during three months.[2] Two to three years are required for the culms to harden.

Areas of wild small bamboo in the Philippines with an average height of 43 feet in one season are known to yield enough material to make 7 tons of pulp per acre, the cost of which for cutting and transporting by admittedly crude methods is $1.25 per ton. A calculation of the acreage necessary to produce from this source 7,500,000,000 gallons of alcohol (the estimated equivalent of the present annual consumption of 4,900,000,000 gallons of crude oil) is included in Table I. These figures are crude and are given only to indicate the possibilities. Unfortunately we know little or nothing concerning the areas of bamboo in the tropics. In the eastern tropics it is found in pure stands or mixed with hardwoods over vast areas, while in the western tropics it is of very limited occurrence.

Table I—Yield from Small-Sized Bamboo Forests in the Philippines[2,3]

Average yield per acre of dry material	14 long tons
Average yield per acre of pulp	7 short tons
Estimated average yield per acre of alcohol @ 40 gallons to ton of pulp	280 gal.
Acreage necessary to produce heat equivalent to 1920 production of gasoline in United States	27,000,000 (42,200 sq. mi.)
Amount of alcohol from this area	7,500,000,000 gal.
Acreage necessary on 3 years' rotation	81,000,000 (126,600 sq. mi.)
Average cost of raw material per gallon of alcohol	$\$0.03\,{}^{1}/_{8}$

If we are to depend on bamboo for paper pulp or for alcohol, planted crops must be raised. A rough estimate of the cost of bringing them to maturity (5 years) is about $26 per acre, but when once established and properly managed such plantings could be made to yield crops indefinitely.[3] The yield per acre might perhaps be doubled and the acreage reduced one-half by selecting larger species. It is of interest that in the Philippines alone there are some 68,000 square miles of cut-over waste lands in grass and second growth forests that might be made available.

NIPA PALM—While alcohol can be obtained from the inflorescent stalk of many palms, the nipa seems to be best adapted for its commercial production, because, in the first place, it is grown in pure stands as part of the mangrove swamps of the tidewater regions throughout the Indo-Malay region. Secondly, it has no distinct above-ground stem, and its flower stalk is near the ground; consequently the alcohol can be collected easily and cheaply. The plant reaches maturity in 4 to 5 years. Without going into the different items in detail, Table II will show the yield per acre and costs of the raw material per gallon of 90 per cent alcohol.[4,5,6]

Table II—Yield and Cost of Alcohol from Nipa Palm

750 plants per hectare that can product sap
43 liters of sap per plant per season
32,250 liters of sap per hectare
6.5 per cent of sap = alcohol
2096 liters of alcohol per hectare = about 210 gallons of alcohol per acre
Cost of raw material per gallon of alcohol, 12 cents

One distillery (1911) was actually producing 93 per cent alcohol at a cost of about 20 cents a gallon on a 12-hour basis. If run 24 hours, it is estimated that this plant could produce alcohol at a cost of about 15 cents per gallon.[6]

The annual production of nipa alcohol in the Philippines is near to 3,000,000 gallons and only a small part of the entire area is under production, part of which is planted. The largest continuous area of nipa palm in the Philippines is about 22,000 acres. Unfortunately no data are available concerning the total acreage. Much more extensive areas are known to exist in Borneo, and the lumbering concern mentioned above is planning to utilize these for the production of alcohol. To equal the equivalent of 5,000,000 gallons of gasoline produced in the United States in 1920 would require an area of more than 50,000 square miles. If all the tidal swamps of the Indo-Malay tropics were planted to nipa the area available would probably fall far short of this. Nevertheless the possibilities of utilizing the present areas and enlarging them for the production of alcohol is worth considering.

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[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] W. H. Brown and A. F. Fisher, "Philippine Bamboos," Bureau of Forestry, Manila, P. I., *Bulletin* **15** (1918).

[3] G. F. Richmond, "Philippine Fibers and Fibrous Substances. Their Suitability for Paper Making," *Philippine J. Sci.*, **1** (1906), 433, Part II, **1**, 1075; Part III, Sect. A, **2** (1907), 81; Sect. A, **5** (1910), 233.

[4] W. H. Brown and A. F. Fisher, "Philippine Mangrove Swamps," Bureau of Forestry, Manila, P. I., *Bulletin* **17** (1918).

[5] W. H. Brown and E. D. Merrill, "Philippine Palms and Palm Products," Bureau of Forestry, Manila, P. I., *Bulletin* **18** (1919).

[6] H. D. Gibbs, "The Alcohol Industry of the Philippine Islands. Part I," *Philippine J. Sci.*, Sect. A, **6** (1911), 99.

WILD GRASSES—About 40 per cent (48,000 square miles) of the deforested area of the Philippines is covered by two wild grasses, *viz.*, cogon (*Imperata exaltata*), known in other parts of the Malay regions as langlang grass, and talahib (*Saccharum spontaneum*). Experiments indicate that these, especially cogon, compare very favorably with esparto grass in regard to yield of pulp, averaging about 45 per cent by the soda process. The cogon is a grass 5 or 6 feet in height and is found in the drier soils, while talahib, found in the damper soils, reaches a height of 9 to 10 feet. In some parts these grasses could be made to yield two crops per year. Unfortunately, no figures are available for their average acre yield.

In other parts of the tropics there are large areas covered with grasses that might be suitable for paper making and possibly alcohol, among which may be mentioned the cana brava (*Gynerium sagittatum*), a large bamboo-like grass found throughout the moist tropical climate of America. It is cultivated in many parts, especially Columbia and Venezuela, for construction purposes.

AGRICULTURAL CROPS

Unfortunately, reliable average statistics concerning the cultivation in tropical regions of strictly staple agricultural crops are not available. The figures given below are therefore subject to correction as additional information becomes available.

CASSAVA (*Manihot*)—Cassava is a woody plant 4 to 10 feet in height whose roots contain large quantities of starch. Crops can be grown in 6 months, but the best results are obtainable from 9 to 11 months. Figures on the yield per acre vary greatly, but reliable figures from Florida,[7] British Guiana,[8] and Brazil,[6] indicate 10 tons per acre as an average. This would vary according to soil conditions. According to the Imperial Institute,[9] the yield per ton is 30 to 35 gallons of 95 per cent alcohol. The cost of the raw material in Florida before the war, delivered at starch factories, was $6.00 per ton, but in tropical regions it is probably much lower than this. Costs and yields are tabulated in Table III.

TABLE III—COST AND YIELDS OF CASSAVA

Yield per acre of roots	10 tons
Cost of raw material per ton	$5
Per ton yield of alcohol	30 gal.
Per acre yield of alcohol	300 gal.
Cost of raw material per gallon of alcohol	$16^2/_3$ cts.
Acreage necessary to raise the equivalent of the 1920 production of alcohol in U. S.	27,000,000 (about 40,000 sq. mi.)

It is the author's opinion that of all agricultural crops this is one of the most promising to investigate for the production of immense quantities of alcohol, since with improved methods of cultivation the yield per acre could undoubtedly be increased considerably.

CORN (MAIZE)—This crop is extensively raised in the tropics but exported to only a slight degree. Mexico stands next to the United States in acreage of corn, but follows Argentina in actual amount produced. The average production per acre in the United States is about 25 bushels, in Argentina (not tropical) it is 27 and in Mexico (mostly highlands) it is 14 bushels; the methods of cultivation, however, in the last named are not conducive to high yields. In British Guiana, where 4 months are necessary to raise a crop, 18 to 25 bushels per acre are said to be the yield.[7] Possibly two crops per year might be raised. With a production of 50 bushels, the same amount of corn would be raised in the tropics as in the United States, on an area one-half that in our own country. This high rate of production would seem somewhat problematic in view of various factors operating against it.

RICE—In the tropics the rice crop usually takes four to five months to mature. Where the rainfall is sufficient it can be grown without irrigation. It is probable that if the proper amount of soil moisture could be had, say by irrigation, two crops per year could be obtained.

COTTON—While cotton is of tropical origin, most of the world's production comes from the North Temperate region. Continuous rainfall and much cloudiness is detrimental to growth of cotton; hence very moist tropical regions are not suited to its production. In regions subject to drouth irrigation is necessary. While there are many extensive regions in the drier parts of the tropics that could be made to yield larger amounts than they are now doing, it is probable that the production per acre in the tropics cannot be increased over that of the best portions of our own cotton belt.

SUGAR CANE—This is essentially a perennial crop. In Cuba and the tropics five to ten crops are, in general, obtained from one planting, fully twelve months or more being necessary for the maturity of a crop. In Louisiana the best yields are obtained by planting annually or biennially since winter frosts damage the stubble; hence varieties must be chosen which mature in six to seven months. Black-strap molasses from refining sugar is the present source of most of our industrial alcohol.

SUMMARY

The above is an incomplete review of the possibilities of the tropics to produce crops of foodstuffs and wood capable of application to the manufacture of cellulose and alcohol. Little or nothing is known of the possibilities of many of the wild forest products for the manufacture of pulp suitable for paper making, or the amount of alcohol that they will yield by distillation or by fermentation processes. Until we find fast growing species suitable for these purposes it is nonsense to talk about producing them on a large scale. The few figures given serve merely to indicate the possibilities and are based on admittedly limited data

The evidence, however, is conclusive that the tropical sun has the power to store up more energy in the form of cellulose in a given time than has the temperate sun, and if this is in a utilizable form it remains for the ingenuity of man to overcome the difficulties of profitably applying it.

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[7] S. M. Tracy, "Cassava," U. S. Department of Agriculture, *Farmers' Bulletin* **167** (1903).

[8] J. B. Harrison, "Food Plants of British Guiana," *J. Board of Agr. of British Guiana*, **10** (1917), 143.

[9] "Cassava as a Source of Industrial Starch and Alcohol," *Bull. Imperial Institute*, No. 4, **17** (1919).

American Metric Association

The American Metric Association held its annual meeting in Toronto, Canada, December 29, 1921.

The Canadian members present were unanimous in the opinion that the passage of an effective metric bill by the United States Congress would soon be followed by similar action in the Canadian Parliament. Prof. Henry G. Bayer of New York University discussed "The Evolution of Metric Weights and Measures." Edward Richards and other members of the Society of American Foresters spoke on the "Application of the Metric System to Forestry." Prof. E. C. Bingham reported that through the coöperation of the Association with the American Chemical Society and other organizations three hundred of the universities and colleges had agreed to order their supplies in metric units. Manufacturers and dealers have been found very willing to fill orders in this manner.

The Technical Paper and Its New Relation to Industry[1]

By H. C. Parmelee[2]

New York, N. Y.

If we attempt to analyze the elements that have contributed to the evolution of modern civilization in all its variety and complexity, we are likely to come to the conclusion that the most powerful single force has been the rapid development in the means of communication between individuals, communities, cities, and nations. To such a degree of perfection have these means been developed, and so complete has been their conquest of conditions on our own earth, that intrepid pioneers are already attacking the problem of interworld communication.

Great industries have been founded in the course of these developments. Ships sail the seven seas to the uttermost parts of the earth; railroads cover the continents like networks of steel; aircraft cruise their routes regularly with incredible speed; the telephone and telegraph are known in the humblest village; radio communication is almost a commonplace; and finally the products of the printing press have long since lost the element of novelty and are accepted as an integral part of our daily life. These agencies have brought about the great transition from primitive society in which human intelligence was transmitted by word of mouth. They have at once simplified and complicated modern life; simplified it by bringing the peoples of the earth into closer contact, and complicated it by extending our relationships and increasing our duties and obligations. They have unified nations in war for a great cause, and they have given an impetus to peaceful industrial growth unparalleled in the history of the world.

But though all these agencies have contributed largely to the development of modern society, it is certain they have not been of equal value and importance. Ships, railroads, and aircraft may be developed ever so highly and yet be limited as means of communication if they transport only men from place to place. Important as are the telephone, telegraph, and radio in the quick transmission of intelligence to and from all parts of the world, they are still restricted to communication between fixed points and a small number of individuals. Obviously some other agency in combination with these has been responsible for that wide distribution of human knowledge and intelligence that characterizes modern society and which has been responsible for its development. Some other means has been evolved to reproduce for thousands and millions of individuals the product of the world's great intellects and lay it regularly before all who want it. It is in the discovery and perfection of printing and paper that we find the essential element in all this marvelous development. Modern civilization, said Lord Avebury in addressing an international gathering of paper manufacturers, depends upon the discovery of cheap paper and rapid printing for the wide distribution of information.

This we may accept without demanding exhaustive proof, for it requires no stretch of the imagination to visualize the influence of printing on the wide dissemination of knowledge. By this means industrial, political, and economic information has spread with amazing rapidity. By it the intelligence of one nation has become the property of the whole race, and the intellect of a great leader has been able to influence the trend of thought of the entire world. In short, we may accept the press as the means of communication par excellence and proceed to examine one of its comparatively small but important branches, namely, the industrial press, that has just begun to sense and exercise its power.

Industrial publishing has reached its highest development in the United States, where over 1200 periodicals are now devoted to industry in all its phases. The growth of this great publishing business has been coincident with the industrial expansion of the country itself. The first industrial paper of which we have record in this country was founded in 1846. In the next decade two more were established, but no great impetus was given to the business until after the Civil War when the country went through its marvelous period of growth and development. Industries of all kinds invited leadership, and industrial magazines sprang up to point the way. The result was that from one paper in 1846, three in 1856, and 25 in 1869, the number grew to 800 by the end of the century and to well over 1200 at the present time. Including Canada, it is estimated that there are in America between 1200 and 1400 industrial publications, the number varying with the method of classification.

An important group of the industrial press comprises what are known as technical papers because they deal with the technology of industry, with the application of science and engineering principles to the problems of production and management. It is in this group that you, as chemists, are most interested; and since both you and I have a still narrower interest in technical magazines devoted to the chemical industry we may confine further observations to papers of that class.

The Technical Paper of the Earlier Day

My topic, "The Technical Paper and Its New Relation to Industry," suggests a contrast with an earlier relation, and so we may go back for a moment and sketch that former relation briefly so as to emphasize the new order that must be expanded and developed if the technical paper is to live up to its opportunity for service and leadership.

Technical papers for the chemical and allied industries are of comparatively recent development in this country, but if we examine the early files of such papers we will find that they were devoted almost strictly to matters of technical interest. They recorded the results of scientific research and investigation and of progress in the arts. Processes and products were discussed in their scientific and technical aspects. The contributions were of a high order of merit, and the contributors were recognized scientists of learning and ability. On the whole the publication was maintained on a high plane of scholarship and was a credit to the profession. Its reliability and integrity were above reproach and its subscribers bore testimony to its value and influence in all technical matters. It was a tool of the profession rather than of the industry.

The *raison d'être* for such a magazine is not far to seek. It was a product of its time and it served its purpose well. Technical industries were in a state of rapid evolution, and the latest developments in technology were of primary importance. It was essential that the scientific foundation of industry be carefully laid in order that the superstructure might endure. In short, industry being more interested in, and most in need of, technical leadership and guidance, the function of the technical paper was plainly to serve along these lines.

The New Responsibilities of the Technical Press

But excellent as this service was, and adequate though it proved for its time, it will not suffice to-day. New elements have entered into our national industrial life and, by presenting new problems to industry, have at the same time laid new and additional responsibilities on the technical paper. It is no longer enough for it to treat of technology; it must consider the business and economic problems of industry as well. The technical paper can no longer fulfil its function if it merely discusses processes and products; it must also be the business exponent and mouthpiece of its industry, reflecting its needs and guarding its interests. It must become an integral part of its industry, serving all its needs. It must be of the industry as well as for it.

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[1] Presented before the Chicago Section of the American Chemical Society, November 18, 1921.

[2] Editor of *Chemical and Metallurgical Engineering*.

The perception of this new responsibility was quickened during and immediately after the war, when we faced industrial and economic problems that far transcended in importance the problems of technology. The Government itself was confronted with industrial problems of the greatest magnitude, and as a result of the war was involved in the most intimate relations with business and industry. There was the greatest need for some public agency to reflect the needs of industry to the Government and to interpret the intentions and acts of the Government to industry. In this condition industry found itself without a mouthpiece or exponent unless the technical press threw itself into the breach, which it promptly did.

Washington became a great center for technical and industrial news, requiring the closest daily contact on the part of the business press; and as a consequence of the early recognition of this fact, industry was served with pertinent government news through its technical papers.

The necessity for this arose mainly from the fact that the daily press in all its excellence was not equipped to meet the need. It was not and could not be intimately familiar with the details of industry, and consequently could not sense its needs. The whole country was face to face with a brand new crop of problems, and since industry had learned to follow its own technical papers in matters of science and technology it naturally turned to the same source for leadership in these new conditions. The technical paper promptly sensed and accepted the situation. It became a magazine of opinion on labor problems, on the tariff, on wages, on the cost of living, foreign trade, government policies, the patent system, revenue legislation and finance, and many other matters formerly regarded outside its editorial scope. It discussed industrial waste in all its forms; the necessity for better cost accounting, for greater safety in industry, for improved housing and sanitation, for more skilful management, for more research. It expressed its opinion on the regulation of business by the Federal Trade Commission and the Interstate Commerce Commission. It took up industrial relations between employer and employee and devoted much space to the numerous phases of that many-sided subject. It spoke with authority and competence on such matters as reorganization of government departments because some of its editors had been drafted from government service and knew whereof they spoke.

These things were invaluable because they reflected to the industry the opinions of men familiar with the industry itself and sympathetic with its needs. Speaking from a chemical point of view, it was not enough to discuss the technology of the industry; somebody had to present the economics as well. For example, coincident with the technical problem of fixing nitrogen was the question of government ownership and operation of nitrate plants and its effect on business. Of quite as much importance as how to make dyes was the question of establishing an industry in the face of foreign competition. The tariff was a paramount issue. We had the brains for dyemaking, but we needed the economic basis for an industry without which our technical brains would avail us nothing. The alcohol industry likewise was, and is, much more concerned with fanatical legislation than with methods of manufacture. All of these things were consistently presented in the technical press for the benefit of industry and the education of government officials.

In the matter of new developments there was the constant necessity of keeping the economic and industrial as well as the technical aspect clearly in mind. For this reason the technical press has brought to industry vital statistics on consumption and production, on imports and exports. It has shown the close relation of plant location to industrial success. It has featured the importance of markets for new products and sources for raw materials. It has acquainted industry with pertinent activities of the Government, sometimes approving and sometimes condemning.

In its relation to the Government the technical paper has been constructive and helpful. Witness its service since the war in aiding in the disposal of surplus property; in suggesting new uses for materials held in large quantities by government departments; in discussing the function of the Government in research; in advocating reform in the Patent Office; in supporting the Chemical Warfare Service and creating public sentiment that resulted in establishing this branch of the service on a scale somewhat commensurate with its importance.

Probably the greatest stimulus to this new function of the technical press as an intermediary or connecting link between the Government and industry was the action of Mr. Hoover in inviting the editors of the business press of the country to assist him in solving many of the problems with which he was confronted in the Department of Commerce. This was at once the greatest recognition of the importance of the industrial press and a challenge to prove its usefulness by showing its intimate knowledge of industrial matters. What body of men in the country should be better able to reflect to the Government the needs of industry, and carry to industry the story of the Government's intention to aid and assist rather than hamper and restrict? So argued Mr. Hoover, and accordingly the memorable Hoover editorial conferences began in Washington last spring and have become a monthly event. They have resulted in laying before the Secretary of Commerce plans for elimination of waste, for standardization of sizes, types, and styles of industrial products, for correlating the bureaus and agencies in his department and making them function more directly for the benefit of industry. They have resulted in the first effort ever made in this country to publish monthly vital statistics on consumption, production, and stocks of critical commodities in the basic industries. Finally they have been helpful in the reorganization of the Department of Commerce by finding men from the industries to head the new commodity divisions that have been created. And all of these things, mark you, have been done by technical industrial papers that formerly devoted themselves wholly to matters of science and technology, because they have seen clearly the need of this new service to their respective industries. Much of the best work has been done quietly through committees, questionnaires, and researches, but it has been none the less effective. Mr. Hoover has generously recognized the value of this service in a message to the editors, in which he said in part:

> The editors of the business press have shown a fine spirit of service. Your opportunity for leadership is unique and unchallenged. Upon you rests in large measure the responsibility of the control of industrial thought and opinion in the detail of the industrial, economic and technical problems which confront us.

Limitations of the Daily Press

I have mentioned the inadequacy of the daily press in presenting to industry such matters as have just been discussed. They are essentially technical and hence not within the grasp or province of the daily newspaper. They will not be adequately presented for business and industry except through the medium of the industrial press. This is no reflection on the daily press but merely a recognition of its limitations and the consequent need for the industrial press. We may consider a few examples.

As an industrial disaster the explosion of the nitrate plant at Oppau, Germany, was of such magnitude as to interest the entire world. And because of its marvelous mechanism for transmitting intelligence, the daily press gave us immediate reports of the occurrence. But the explosion had a far greater and deeper significance to chemical industry, and in all its attempts to give precise information that might be helpful the daily press failed utterly, as a result of its manifest limitations. Not only did it fail as a purveyor of precise, accurate, and reliable technical news of the event, but it exemplified the blind as leaders of the blind in its editorial comment. So great a newspaper as the *New York Times* drew the conclusion that German chemists had been experimenting with new and deadly gases, in violation of the terms of the treaty, and had wrought their own destruction through their discoveries. It called upon the Badische Company to show clean hands in the matter, and it looked frankly with suspicion on the whole affair. Mystery surrounded the explosion and consequently mysterious conclusions were drawn as to its cause and significance. The press dispatches having said that the disaster was due to "the decomposition and subsequent explosion of a large quantity of ammonia and sulfate of saltpeter," the *Times* suspected "experimenting of a secret nature," and thought it "not inconceivable that the disaster at Oppau may have been due to covert experimenting by those chemists." All of which was of no help or consequence to the chemical industry, and it devolved upon the technical press through its enterprise and intelligence to inform the industry of the facts as nearly as they could be ascertained.

Another instance of the newspapers' inability to serve industry in technical matters is to be found in the attitude of the daily press toward the coal-tar industry. We may take as typical the editorial comment in the *Rocky Mountain News* of Denver, September 30, 1921, on "The West and the Coal-Tar Industry." The caption of the editorial immediately suggests a narrow sectional view of the proposed embargo on the importation of coal-tar products; and this is confirmed when we read later on that "if it can be shown that the fortified industry in time can reach out and make useful the coal deposits of Colorado, naturally Colorado would take more interest in the issue at Washington." No broad view of the coal-tar industry as a factor in national welfare. No conception of it in its relation to the other industries using dyes. No recognition of the fact that disarmament could proceed much more rapidly and taxes be reduced proportionately if the United States and all the nations each had a well-established coal-tar industry functioning in peace and guarding against war. Instead a small, sectional, wholly inadequate view of the matter. And yet the daily press regularly creates public opinion through pronouncements as incompetent as this.

Examples might be multiplied. Chemical warfare was first condemned in the daily press, and first supported by the technical paper. Reports of such conventions as President Wilson's first industrial conference and the recent unemployment conference were more reliable and pertinent in the industrial than in the daily press, for the reason that the latter was inclined to feature spectacular incidents and subordinate substantial accomplishments.

All of these things are in the nature of a service to industry and the public welfare now performed by the technical press. It is not spectacular, but far-reaching. It influences the intelligent leaders of industry to blaze the way to new reforms, initiate constructive policies, and establish sound principles and practices in industry.

This service to industry by the technical press is a leaven that eventually leavens the whole of society. Through the leadership of the technical magazine in its own industry, it spreads information and serves as a clearing house for new ideas that eventually are translated into economies for the benefit of society as a whole. The service to industry is direct, and to society indirect.

The Functions of the Technical Paper

From this general portrayal of the activities of the modern technical paper we may proceed to summarize its functions in industry and study the mechanism through which they are performed.

1—The modern technical paper is still a magazine of information pertinent to the technology of the industry it serves. This is an important function that cannot be subordinated without jeopardizing industrial progress. Economies resulting in cheaper production must still be worked out through scientific research and the application of the results in the factory. But this is not service enough.

2—The modern technical paper also treats of the economics of its industry, informing its readers on the relation of finance, the tariff, and other legislation to business.

3—It is the newspaper of its industry, gathering weekly the items of personal and business intelligence on which its readers should be informed. Market movements and trade tendencies are reflected in reports gathered at first hand. Foreign as well as domestic news is obtained regularly by cable and wire.

4—The modern independent technical paper is a magazine of opinion—the mouthpiece of its industry. And herein lies one of the distinctive differences between it and the technical society magazine. The editorial independence of the industrial paper, its freedom from domination by any interest or allegiance to any group, makes it possible to adopt policies in the interest of the industry as a whole. Obviously this is denied to the society publication, which must serve primarily its own membership. Editorial opinion cannot be expressed with freedom on a wide variety of topics for the evident reason that the magazine must speak for the society. An independent industrial technical paper, on the other hand, labors under no such handicaps, being bound only to serve the best interests of its industry whether people agree with it or not. If subscribers do not like its policy they need not take the paper.

5—The modern technical paper sets a high standard of business ethics and practice in its industry. Both in its business and editorial departments it subscribes to a code of ethics that has been adopted by associations of business publishers and industrial editors. These standards are high and must be subscribed and adhered to by members of these associations.

The technical editor is pledged to consider first the interest of his subscriber. Truth and honesty must characterize his every activity. He is obligated to present the news of the industry free from personal bias and to determine the editorial contents of his paper independently of advertising considerations. The publisher also sets a high standard of business practice in the acceptance or rejection of advertising and in publicity regarding the character and extent of his circulation.

Periodical investigations are made to see that members are living up to these standards. This is one of the most powerful factors in making the technical paper a leader in its industry. With its own skirts clean it can consistently demand that its industry be free from unfair practices. Having adopted a high code of business ethics for itself it can, both by precept and example, urge similar action upon its industry. The adoption of a code of editorial ethics and business practice has been of the greatest benefit in establishing the independence of the technical paper.

The exercise of all these functions results in a service, first to industry and then to society, that makes the modern technical paper an essential element of industry. It was so regarded by the Government during the war; and it must be self-evident that in times of peace, publication of knowledge and intelligence is indispensable to the development of industrial literature. What, then, is the mechanism for exercising these functions? The answer is found in the editorial staff. And just as the technical paper's new relation to industry requires a broader service, so the modern editorial staff comprises a wider range of talent. In many respects it resembles a college faculty, being composed of men who are specialists in their respective branches of technology and industry. Papers covering the chemical and allied technical industries find it particularly necessary to have comparatively large staffs of qualified scientists, technologists, economists, and industrial experts. They are called upon to judge the competence of articles that form our technical literature. They are expected to reflect sound opinion on matters of public policy in relation to their industries, and to take the lead in safe-guarding those industries from ill-advised legislation or private practice. They must display enterprise and initiative in discovering sources of news and information so that their industries may be kept abreast of developments. And it goes without saying that in addition to their ability they must be men of integrity with a keen sense of editorial ethics.

Nor can these things be accomplished without close personal contact with the industry itself. Travel by the editors is a *sine qua non* of successful industrial journalism. Conventions must be covered and reported in their essential features, for hundreds and thousands of men are unable to attend and must rely on the published record for their information. That this service is appreciated is attested by the correspondence following the publication of convention proceedings, asking for more detail or further information. Plants must be visited and processes described in order that textbook fundamentals may be amplified and brought up to date with practical details of current practice. In short, the modern technical paper cannot be edited from the desk, but it must show a familiarity with industry itself that is acquired only by personal contact. The consequence is that the industrial editor is enabled to see his industry as a whole and judge it impartially. This was strikingly exemplified at the last National Conference of Business Paper Editors in Chicago, when a résumé of conditions in ten basic industries was presented by as many editors of industrial magazines. These reviews were authoritative and could not have been pictured better, if as well, by industrial leaders themselves.

Such, then, is the new relation of the technical paper to industry, as seen by the technical editor. Such is the duty of the industrial and technical press, as well as its opportunity for service, as conceived by the publishers. It results in a service that is growing more and more expensive, but which yields results to industry that more than justify the publisher's outlay. No single industrial unit could afford to maintain for itself the service thus rendered to industry at large. It is a service that is destined to be expanded rather than contracted, just as industry itself becomes more complex and needs broader vision and leadership.

This evolution holds its lesson also for the individual. Just as the technical paper must supplement its technology with the economics and business of industry, so must the individual broaden his scope in order to find his greatest usefulness. Science will never develop its greatest usefulness to society as long as it is translated into technology only. It must find expression also in sociology, in economics, and in the management of industry. This will call for broader training and more diverse talents among scientists, some of whom will continue to enrich the records of research while others develop managerial ability or technical superiority or acquire skill in the practical application of economics and sociology. The ultimate aim—for the individual as well as for the industrial press—will be the perfection of our industrial processes, the elimination of waste, the stabilizing of labor and production, so that human happiness and standards of living may be increased. To such an end the modern technical paper is dedicated.

The Field for Chemists[1]

By Wilder D. Bancroft

War Memorial Professor of Chemistry, Cornell University, Ithaca, New York

Chemistry is the science which deals with all properties and all changes of matter that depend on the nature of the substances concerned. According to this definition,[2] which is broader than the usual one, chemistry is the fundamental and dominant science, which may account for its being the most fascinating one. Chemistry, as thus defined, may be interpreted to include all of what is known as physics except the law of gravitation, the laws of motion, and a few other abstract formulations. Everything else that gives life and interest to physics is chemistry by definition. Our friends, the physicists, look upon physics as the fundamental science because physics was a well-developed subject before there was any scientific chemistry worth mentioning. This method of reasoning is natural but not necessarily sound. As children we were told that great oaks from little acorns grow. This is true but not the whole truth. If we have only the acorn, it is, of course, the important thing; but, later, one sees that the acorn is merely an interesting subdivision or product of the oak.

Engineering is largely applied chemistry. If it were not for the specific properties of iron, copper, concrete, brick, and all the other materials of engineering, there would be no such subject as engineering, which, speaking broadly, is the art of making the structural properties of matter available to man.

In the biology of the present and the future, we are interested in the chemical changes in the living organisms due to heredity and environment. Growth is a chemical change and the internal and external structures are the result of a series of chemical changes. After the first stages of identification, enumeration, and classification have been passed, the interests of the biologists are largely chemical, and the closer the contact with chemistry the better the results. This has been shown very clearly in the brilliant work of Loeb and his pupils; and Clowes has made it clear that Loeb's results as to the antagonistic action of sodium and calcium salts on protoplasm can be duplicated in a remarkable way with oil and water emulsions.

In curative medicine we are dealing largely with the action of drugs. In preventive medicine we are dealing largely with inoculations, diet, exercise, and fresh air. In the first case we are checking and eliminating an abnormal chemical process, sickness, by the action of one set of chemicals on the system. In the second case we are preventing the occurrence of a disturbing chemical process, sickness, by the action of another set of chemicals on the system. Owing to the difficulties involved and to the number of variables concerned, our knowledge of the chemistry of medicine is not yet what it should be; but it is clear that real progress will be made just in so far as we study physiology and medicine as subdivisions of chemistry.

Geology is the study of the chemistry of the earth, and agriculture is clearly a subdivision of chemistry. The fertility of the soil and the growing of crops are chemical problems in spite of the fact that they have been studied empirically for centuries.

Professor Stieglitz of the University of Chicago has said that chemistry makes possible the scientific control of such widely divergent industries as agriculture and steel manufacturing.

> It governs the transformation of the salts, minerals, and humus of our fields and the components of the air into corn, wheat, cotton, and the innumerable other products of the soil; it governs no less the transformation of crude ores into steel and alloys which may be given practically any conceivable quality of hardness, elasticity, toughness, or strength. Exactly the same thing may be said of the hundreds of national activities that lie between the two extremes of agriculture and steel manufacture. Moreover, the domain of the science of the transfor-

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[1] Prepared January 1921. Received November 7, 1921.

[2] *Science*, [2] **27** (1908), 979.

mation of matter includes even life itself as its loftiest phase. From our birth to our return to dust, the laws of chemistry are the controlling laws of life, health, disease, and death. The ever clearer recognition of this relation is the strongest force that is raising medicine from the uncertain realm of an art to the safer sphere of an exact science. To many scientific minds it has even become evident that those most wonderful facts of life, heredity and character, must find their final explanation in the chemical composition of the components of life-producing, germinal protoplasm; mere form and shape are no longer supreme, but are relegated to their proper place as the housing only of the living matter which functions chemically

Research Problems in Pure Chemistry

The student who wishes to take up research work either in pure or applied chemistry can find innumerable problems in every field and of any degree of complexity and importance, from work that can be done by an undergraduate to work that no one sees how to do at present. No matter where we turn, we find that we have only touched the fringe of the subject. A few illustrations may be helpful. To those in the Chemical Warfare Service, the war brought out clearly the meagerness of our knowledge even in regard to the simplest organic compounds. It would be quite impossible to-day to write a satisfactory monograph showing the reversible equilibria between the compounds of carbon, hydrogen, and oxygen, even if we limited ourselves to compounds containing not over three atoms of carbon to the molecule. If we went as high as compounds containing six atoms of carbon, our monograph would consist chiefly of gaps.

The whole problem of chemical affinity as applied to organic compounds is in a very rudimentary state, and while we are accumulating data in regard to free energy, our progress is very slow. The Periodic Law is still very much of a mystery to us and we do not know why a consideration of the atomic numbers removes some of our troubles. We know a good many facts about catalysis in general and contact catalysis in particular; but we have no adequate theory on the subject, though the poisoning of catalytic agents is not the mystery it once was. While several books and innumerable articles have been written on the subject of indicators in quantitative analysis, nobody has collected the facts that the analyst really wants.

When it comes to color, we speak learnedly of chromophoric groups; but we do not know why anhydrous copper sulfate is colorless, why a solution of copper sulfate in glycerol is green, or why the absorption spectrum of a concentrated copper bromide solution is very closely the sum of the absorption spectra of a copper sulfate solution and liquid bromine.

The organic chemist finds an enormous amount of scientific work still to be done in connection with the synthesis of dyes. The whole field of chemotherapy is just opening up. The problem of plant synthesis has scarcely been touched. We can make in the laboratory many of the substances which the plant makes. Some of them, such as alizarin and indigo, we can make more cheaply than the plant can and of a higher degree of purity; but we cannot make any of them in the way the plant does. The plant does not use reverse coolers or sealed tubes; it does not boil with sulfuric acid or fuse with caustic potash; it has not metallic sodium and chlorine gas for reagents. The reagents on which the plant can draw are air, water, and a few mineral salts. With these and under the influence of heat, light, difference of electrical potential, and enzymes, the living protoplasm manufactures its product.

While the general theory of photochemistry is quite simple—that light tends to eliminate the substances which absorb it—our knowledge of the chemistry involved is so limited that we cannot actually treat photochemistry scientifically. We have made no progress in the direct utilization of the sun's rays and, while we think we know something about the conditions for chemiluminescence, we cannot produce cold light even though the firefly has shown us that it can be done.

Technical Problems

On the more strictly technical side, the problems are so numerous that it will only be possible to indicate a few. If our present civilization is to pull through, the scientific man must speed up production of crops and goods so that the masses of the people can live decently. While everybody will have to help in this, the bulk of the strain will come on the chemist and he must be prepared to meet it. We appreciate already the importance of nitrogen fixation and of getting potash from feldspar. The whole question of the better utilization of our petroleum resources is a vital one. Fortunately this has been realized by the oil producers and consumers, and Dr. Van H. Manning, formerly Director of the United States Bureau of Mines, has been appointed Director of Research of the American Petroleum Institute, which means that this work will be pushed as rapidly as possible. The American Institute of Baking is trying to improve the quality and keeping power of bread. The use of flotation processes has made it possible to work ore deposits which otherwise could not be handled profitably. The statement has been made that sixty million tons of ore are treated annually by these processes in the United States. While this is very gratifying, the development has been largely empirical so far, and we apparently have no realization as yet of the possible future applications of these processes.

When we consider ceramics, rubber and other plastics, paints, varnishes, leather, dyeing and printing, cellulose, cellulose nitrates and acetates, photography, etc., all subjects involving a large amount of colloid chemistry, we find that the industries concerned have a vast amount of empirical information as to what happens and know practically nothing about why it happens. The silicate industries are avowedly empirical and so is the dyeing industry. The rubber industry knows practically nothing about the theory of vulcanization, to take a single illustration. So far as can be learned the people in the cellulose nitrate industry do not even know how many cellulose nitrates there are or what their real properties are. The photographic industry has only empirical knowledge in regard to emulsions and has no adequate theory in regard to photographic developers. Nearly all of the tanneries in the country are run on an empirical basis. While many firms in these various industries have made a great deal of money, all our experience is that every increase in the scientific knowledge of a subject is followed sooner or later by an improvement in the technical processes, and it is certain that the industries in question will prove no exception in spite of the fact that each industry, which is run on an empirical basis, invariably believes that its case is exceptional. The recent work of Dr. Wilson on quebracho and gambier and on the analysis of tannin brings out clearly some of the important things which had been overlooked by the leather industry. All these industries will eventually be put on a sound scientific basis and this work will have to be done by chemists.

Present Position of the Chemist

The general position of the chemist is better than it has ever been before. The war has brought to the public mind an appreciation of the importance of chemistry. Some of the universities have already put their professors of chemistry on a special basis and the others will have to follow suit if they hope to fill vacancies with good men. In most universities the pay of the younger members of the staffs has, very properly, increased more relatively than that of the full professors. There used to be very few research fellowships for men who had received their doctor's degree, but now we have the National Research Council Fellowships in Physics and Chemistry which are open only to applicants who have received the doctor's degree or its equivalent. Some of the universities have similar research fellowships. The du Pont Company is giving a number of unrestricted fellowships open to graduate students, and other companies are doing likewise though not to such an extent.

In the industries the Research Laboratory of the General Electric Company is the best known; but there are a number of other large ones, those of the Western Electric Company, the du Pont Company, the Eastman Kodak Company, the National Carbon Company, The Barrett Company, the National Aniline Company, the Goodrich Company, the Goodyear Company, the Brown Company, and the one of the General Electric Company at Nela Park being conspicuous instances. In addition very many companies are running smaller research laboratories. It looks also as though in the plants the ratio of chemists to engineers was going to increase considerably. Of course, the almost insane demand for chemists that prevailed at the end of the war has ceased and most companies are now discharging chemists as well as other technical men. When the present industrial depression is over, things will adjust themselves and we shall get on a normal basis. It looks now as though the next thirty years would be the period of the chemist just as the previous thirty years were the period of the engineer.

SOCIAL INDUSTRIAL RELATIONS

Charity

By H. W. Jordan

Syracuse, New York

We have just passed through the annual newspaper orgy of vicarious charity in behalf of each city's One Hundred Neediest Families. The lavish expenditure of printer's ink and other folk's money revealed little effort to prevent the return next Christmas of the same families, reënforced by new members and supplemented by other households attracted to the honey of newspaper readers' cash; each donation duly announced in the paper.

One hardship the war brought upon these Neediest Families was jobs. Although the managers of the professional charity organizations succeeded in holding their staffs intact, their clientele dwindled almost to the vanishing point. Plenty of work, lack of drink through prohibition, and diversion of public emotion to the soldiers and of public money to Liberty Bonds, nearly killed the vested interests of organized charity. We came near proving that "Poverty would cease if charity be stopped for a year."

Now that peace rages, the army of constitutionally needy are back in their city trenches. Their crushing cost of maintenance merits serious consideration. Syracuse and other cities have organized Community Chests to handle the collection of charity funds by an annual drive, followed by distribution of the money pro rata to each nice, certified charity.

COMMUNITY CHESTS HAVE A FAR GREATER MISSION THAN THAT OF HANDLING MONEY. They offer an opportunity of doing a splendid social industrial service by applying science through research upon charity, as science has been applied through research to industry. If chemists and engineers can secure appointments on the directing boards of Community Chests they will be able to undertake this sorely needed social study. But if Community Chest management be restricted to captains of finance, with little scientific thought and puny social imagination, who make the Chests mere money feed tanks, they will only aggravate pauperism.

CITY POVERTY IS A SOCIAL BY-PRODUCT OF MODERN INDUSTRY. Specialized employment, herding of people in rented quarters, feeding folks on factory cooked, paper packaged food, complete dependence upon wages or salary for a livelihood with no recourse to farms or villages for partial or temporary relief from unemployment, living conditions that promote tuberculosis, venereal disease and other crowd maladies; these and similar circumstances of city life that spring from modern industry, have forced 15 to 20 per cent of our people below the line of adequate, permanent self-support. Only in times of extremely abundant employment does the percentage fall to 10.

In a herd of livestock if 10 to 20 per cent yielded no milk or wool or eggs, and were unfit for meat, the owner would be bankrupt. No farmer would permit his stock to sink to that low ebb, except through malignant disease or prolonged drought.

Yet industry which depends upon capable, contented labor to produce goods, and on normal thrifty people to consume them is confronted by a population of which one-fifth, on the average, has been surrounded by conditions beyond their individual control, which make them collectively a steadily increasing economic and social dead load; economic because if employed they are incompetent, and if idle they must be fed, clothed, and housed; social because every adult man and woman of them is a persistent voter.

This submerged fifth dominates city elections. They roll up huge metropolitan majorities in election of politicians who cater more and more to the selfish, emotional demands of the ignorant and unthinking. They elect men who vote huge sums in long term bonds for short-lived improvements; men who enact laws of momentary expediency designed to regulate and restrict engineering industry to the verge of bankruptcy.

When the chemical industry, the railroads, the telephone or electric power companies, or other enterprises of modern applied science seek legal enactments in harmony with economic and biological laws we are overruled by these legislators.

IN AN ARTICLE, "PHILANTHROPIC DOUBTS," IN LAST SEPTEMBER'S *Atlantic Monthly*, Mrs. Cornelia Cannon, wife of the distinguished biologist, Walter B. Cannon, discusses the more salient features of social charity. She sets forth the fact that charity does little more than wrap costly sterilized bandages around social cut fingers that would not have been cut if we had whittled away from us. She reaches the conclusion that charity is a practical failure because it is neither constructive, progressive nor preventive. It is merely static.

"Philanthropists belong to the class on which the injustices of our present basis of society have borne lightly," says Mrs. Cannon. "They serve unconsciously as a bulwark of the *status quo*, for whose defects they are ready and eager to apply palliatives. They are the great menders and patchers-up of society, not the surgeons who cut deep into the festering sore and scrape the bone. They express the tenderness and pity of man, not his reasoning intelligence. So long as we placate our intelligence and pacify our consciences by our philanthropies, we put off the day of attack on the sources of poverty."

She urges more effective citizenship of intellectual people, to the end that we root up the causes of poverty.

RURAL AND VILLAGE COMMUNITIES HAVE NO POVERTY OF THE SORT THAT BURDENS INDUSTRIAL CITIES. Modern industry has brought modern poverty. Highly specialized industry has stripped the individual of his resources of individuality, even to the extent that he no longer prepares his own food or shines his own shoes. His amusements have become passive and commercial. Eighteen thousand people sitting, watching eighteen men hired to play baseball, is the national game. Naturally, under these conditions, when life's burdens grow heavy, the individual with minor ambition lies down and lets the community lug his load. And the community competes for the job.

Psychological analysis of the drafted men showed about 15 per cent in Class D, Inferior Intelligence, and 10 per cent more in Class D−, Very Inferior Intelligence—25 per cent in all. These men and their sort, who were not worth shipping to France, are the people that charity fosters and rears. A statistician has figured that at the present rate of increase of the subnormal and the declining birthrate of the rest of us we will all be paupers, idiots, or insane in 267 years.

It is a vital necessity that the industries that arose from science applied to the mechanic arts by chemists and engineers shall undertake similar research to transform the parasitic 20 per cent into self-supporting people.

THE PROFITS OF NINETEENTH-CENTURY INDUSTRY came from exploitation of natural resources and from creation of huge, new industries by applied science—steel, automobiles, moving pictures, talking machines, dyes. All these enterprises were made successful by managers, staff, and workmen who had superior versatility and resourcefulness acquired on the farms and in the villages where they were raised. As these reservoirs of material and human resources are becoming exhausted, the profits of twentieth-century industry must come from correct social adjustment; from elimination of social waste, maintenance of cheap, abundant prime necessaries of life—food, clothing, housing—and modernized primary and secondary education. Unless these social factors be brought into and kept in harmony with economic and biological laws, industry and all thrifty people will be crushed by wages inflated by high cost of simple living, and by confiscatory taxation and legislation that is the legal expression of hostile public opinion of the majority, a majority made chiefly by the incompetent and charity classes, D and D−.

These jaws of the social industrial vise—high cost of living and confiscatory public opinion—are steadily closing in on the railroads, the telephones and upon all public utilities and industrial enterprises in which the savings and life insurance of thrifty people are invested. Unless these forces be diverted into constructive, economic, biological work we chemists and engineers, and indeed all intellectual people, will be smothered by the suffocating forces of mediocrity. It has already happened in Russia.

COMMUNITY CHESTS will be industrial coffins if they be used only to provide money for additional courses on the walls of the already too high reservoir of city poverty and social discontent. But if they supply administrative ability and adequate funds for social scientific research to disclose the causes of poverty and to set the subnormal fifth of our people at steady, productive work, they will be life-buoys for the thrifty and for industry. They offer an opportunity for chemists and engineers to undertake practical citizenship of the highest order.

PERKIN MEDAL AWARD

The sixteenth award of the Perkin Medal was made to Dr. William M. Burton, President of the Standard Oil Company of Indiana, at the meeting of the American Section of the Society of Chemical Industry, held in Rumford Hall, Chemists' Club, New York City, Friday evening, January 13, 1922.

The meeting was unique in that four past presidents of the Society, Drs. Chandler, Remsen, Nichols, and Bogert, were present on the platform. It had been expected that Dr. R. F. Ruttan of Toronto, the present head of the Society, with whom our American chemists became acquainted at the meeting in New York last September, would also be present at the meeting, but he was unable to attend.

In his introductory remarks, Mr. S. R. Church, Chairman of the Section, declared that "seldom if ever has the Perkin Medal Award attracted such widespread interest as has been aroused concerning the present event. In selecting the medalist from a great industry that is outside the narrow classification of chemical industries, the Medal Committee has once more demonstrated a catholic consideration of the problem, 'What constitutes a signal achievement in applied chemistry?' "

Dr. Ira Remsen dwelt on Dr. Burton as a student at Johns Hopkins. He emphasized the essentials of a successful career in chemistry or any other professional activity, as being fundamental knowledge, imagination, courage, patience, and skill. Dr. Remsen called attention to the point which was also stressed by Dr. Herty and Mr. Wiles, that in the case of Dr. Burton we have a chemist recognized as an executive. Dr. Remsen declared that more and more chemists are coming into executive positions, both in educational institutions and the industries, and urged that it is the duty of the chemist to enter into such activities.

Dr. Herty's sympathetic picture of the personality of Dr. Burton, Mr. Wiles' discussion of the future of the chemist in industry as seen by a patent attorney, and Dr. Burton's address of acceptance are printed herewith.

The medal was presented by Dr. Chas. F. Chandler, as Senior Past President of the Society, residing in this country. Dr. Chandler recounted briefly Dr. Burton's industrial career. He became chemist with the Standard Oil Company at Cleveland, Ohio, in 1889, was transferred to the Standard Oil Company of Indiana in 1890, became assistant superintendent of the works in 1892, general superintendent in 1895, director in 1911, vice president in 1915, and president in 1918. Dr. Chandler dwelt particularly on the trip which he and Dr. Burton made to Germany in 1895, as representatives of the Standard Oil Company, to prevent adverse legislation on the part of the German government against American petroleum.

Dr. Burton received the Willard Gibbs Medal in 1918,[1] in recognition of his distinguished work in petroleum chemistry.

The Personal Side of Dr. Burton

By Chas. H. Herty

The charm of biography persists always. The results of a successful man's work are set forth in the public record, whether it be in the form of scientific publications, of official status, of some great engineering feat, of the size of his income tax, or what not. Back of the life accomplishment, however, is the personality of a human being who, following the bent of his own genius, has triumphed over the difficulties which beset us all.

What manner of man did it? That is the question which kindles a different kind of interest from that due to a knowledge of what the accomplishment is. For out of such studies of many types of men we gain here and there suggestions, self-applicable, which help us over our own rough spots and give us hope.

In the case of Dr. Burton, or "Billy," as he was lovingly called by us in student days at Johns Hopkins University, there is added another to the long list of successful men who were born in the country and passed their early days entirely ignorant of cement sidewalks. What a pity we couldn't all have persuaded our parents to move out to the country before we were born. At any rate, it was Billy's good luck to enter the world under such favoring circumstances in the year 1865. In 1886 he graduated from Western Reserve University, receiving the A.B. degree. The next three years were spent at Johns Hopkins University, from which institution in 1889 he received the Ph.D. degree.

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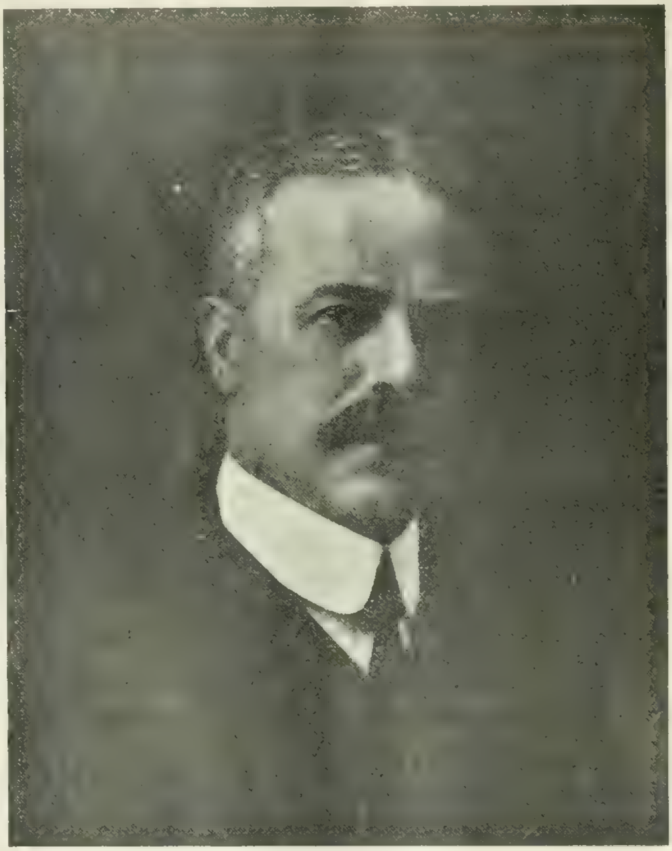
[1] This Journal, 10 (1918), 483.

It is peculiarly fitting that the Perkin Medal should be awarded to him in this the first year of President Harding's administration, for right well does he represent the return to normalcy, all of his friends to whom I have written emphasizing the fact that from boyhood to the present time he has always been a normal individual. He has cultivated no particular hobby, considered by many to be an essential necessary to distinction, but has carried through life a love of experiment and an ardent zest for the lathe and mechanical tools. It is easy to understand, therefore, that in the environment in which he has worked he not only succeeded in cracking oil but carried the work on to a successful application on a large scale.

He plays no outdoor games, not even golf. This sounds abnormal, but to offset it he recently obtained keenest satisfaction in installing in his home under his personal direction a radiator system at one-fifth the estimate furnished by a contractor, and who wouldn't rejoice at getting the best of a plumber? I insist he is normal.



William M. Burton

To him the days of college life and associations are as full of meaning as ever and he wears still his college fraternity pin.

Steadily he has been advanced in that company with which he began work after completing his university training, until to-day he occupies the presidency.

Throughout this advancement he has remained the same sincere, sympathetic, level-headed man to whom his friends and associates come with their problems for his sound advice.

That he has worthily won this great honor from his associates in business all agree, that throughout it all he has preserved his unaffected selflessness all will rejoice; but there is another aspect of his success which deserves not only record here but wide heralding at this stage in the development of American chemical industries. The industry with which he is connected is one of our early and now thoroughly stabilized industries, and it is peculiarly worthy of note that the Standard Oil Company of Indiana has chosen for its chief executive a chemist. Not all chemists are qualified to be executives, but certainly our chemical industries will be placed on a much sounder basis when the chemist of proper qualifications is given opportunity to share in the determination of corporate policies. Billy Burton's record may yet prove the harbinger of a new day.

The Chemist in Industry

By Russell Wiles

The patent lawyer is in a peculiarly favorable position to obtain a bird's-eye view of industry as a whole and of the general tendencies of industrial development. No one is in such close touch with so many industries and certainly no one has had occasion to study the general progress of industry so carefully.

Epochs of Industrial Progress

Industrial progress might be divided into epochs almost as distinct from each other as the paleolithic and the neolithic ages and, like those ages, overlapping each other. The first great stride toward modern industry was the steam engine. To it, for many years, inventors have given their best efforts, but so far as great progress in this field is concerned nothing has been done for years.

The steam engine having supplied power, there followed an immense development of power-driven machinery of all sorts, resulting in the production of old articles at lower prices and countless new articles which it would not have paid to make by old methods. While new machines are still being made, very little of a novel or fundamental character has been done for many years. The principles of machine design are well understood, and it is the commonly accepted belief that an automatic machine can be made, which will do anything desired, providing the demand for its product is sufficiently great to justify machine manufacture.

For the last half century the most conspicuous inventions have been those of the electrician. He has given us the telephone, the telegraph, the dynamo, the motor, the electric light, and countless minor conveniences, the aggregate effect of which has been to revolutionize society. The work of the electrician has not ceased, but the fundamental principles of electricity are quite thoroughly developed and, in the main, progress will probably follow lines which are to-day generally predictable.

Of recent years the development of the internal combustion engine has provided us with many hitherto unknown luxuries, conveniences, and necessities.

The Place of the Chemist

It is only, however, in the last few years that the chemist has begun to take his proper place in industrial development. Great chemical discoveries have been made in the past. Much has been done in chemistry as a pure science, but it is within comparatively recent years that the chemist has emerged from his laboratory and that industry, as a whole, has felt the need of close coöperation with him. Where, ten years ago, big practical applications of chemistry were rare or confined to a few specialized industries, to-day nearly every progressive plant is regularly employing chemical assistance in one form or another, and there is scarcely an industry which has not been more or less affected by the progress of chemical science. Chemical inventions, at least as exemplified in my own practice, are at least ten times as numerous as they were a decade ago.

The work of Dr. Burton may well be regarded as an early example of the great things the chemist is to accomplish in the future, rather than as an achievement which is to be unique in history. The epoch-making inventions of the future will probably be those of the chemist and physicist. It is hard, indeed, in this day of physical chemistry and molecular physics to say where one science begins and the other leaves off. Perhaps it is in the border region common to both that we may look for the most startling discoveries.

The chemist is to-day not only giving us fresh supplies of old products, usually in better and purer form than we had before, and at lower prices, but he is giving us new compounds of every conceivable character with which to rebuild our general industrial structure. The time is not far distant when no engineering undertaking will be complete until the chemist has been consulted to ascertain if the structural materials are the best that can be obtained for the specific purpose. It will be as much the duty of the engineer of the future to build out of the right materials, whether synthetic or otherwise, as to build the right size and shape. The arts are to have available for their use not a few dozen basic materials of which everything must be built but thousands of materials, each having special points of advantage for certain particular uses, and chemical processes are sure to replace many complex mechanical ones. The chemist will revolutionize industry, not once but dozens of times. Indeed, it may well be questioned how long the name of your Society will remain distinctive. I expect to see the day when all industry will be more or less chemical industry.

That the oil industry, as particularly exemplified by the Standard Oil Company of Indiana, has been perhaps the first big established industry to be thoroughly overturned by the work of the chemist, is partly fortuitous—partly due to the remarkable ability of him whom we gather to honor to-night, and partly due to the remarkable organization which he has built up.

It was the discovery of the evil-smelling sulfur-bearing oil in Ohio which forced the chemist into the oil business. Dr. Burton was one of the very first thoroughly trained chemists in the oil industry. His solid groundwork in pure science had been acquired under Dr. Ira Remsen, who, perhaps more than any one else, is responsible for what the American chemist is to-day. Bringing a thoroughly scientific point of view and applying to his problems the methods of pure science, with his great natural ability and indefatigable industry, it was entirely unavoidable that Dr. Burton should profoundly affect the industry in one way if not in another. No man has ever had a more promising field—an enormous industry dealing with problems which ought to be handled in an essentially chemical manner and having no chemists at all. Dr. Burton would be the first to recognize his splendid opportunity, and it is characteristic of him that his opportunity never was neglected.

ORGANIZATION OF STAFF OF STANDARD OIL COMPANY OF INDIANA

But Dr. Burton alone never could have accomplished what has been done by the Standard Oil Company of Indiana. There has been much discussion in big corporations as to the best method of correlating the scientific force with the manufacturing force. All sorts of experiments have been attempted and all sorts of systems have been devised. The system worked out by the Standard Oil Company of Indiana, largely at the instigation of Dr. Burton, and of recent years under his guidance, is unique and amazingly successful. None but a scientifically trained man would have dreamed of such a system, and the operations of the Indiana Company are the best demonstration of the industrial value of scientific training.

The system is founded on the premise that a scientifically trained man is a good man for any job; the scientific staff does not coöperate with the manufacturing staff—it has become the manufacturing staff. The practice, so far as concerns chemists, has been to take on trained men for the laboratory force precisely as in many other plants. After brief association with the laboratory, during which the newcomer can become familiar with the peculiar problems of the works and particularly of some special department to whose problems he is assigned, he leaves the laboratory and goes into the works in some subordinate capacity. It then becomes his prime duty to test, on a practical scale, whatever improvements may fall within the sphere of his department. Having once become established in the works, it has been found that almost without exception the scientific men become excellent executives and their promotion is rapid.

The result is that the manufacturing department of the Company not only maintains an excellent research department, but that the whole manufacturing organization from top to bottom is largely dominated and controlled by men of scientific training. The Standard Oil Company of Indiana is unique in this regard and the tremendous success of its manufacturing department must be very largely attributed to the superb organization which Dr. Burton conceived and has built.

The system has been worked out to the fullest extent at the largest plant of the Company. Let it not be understood that the chemists are the only men of scientific training in the organization. There are more chemists here in executive positions than in any other industry of which I am aware, but along with them are a considerable number of engineers holding equally important positions, and whose coöperation on many problems is vitally necessary. We have become accustomed to finding engineers in executive positions; the Standard Oil Company of Indiana is unique in the number of chemists similarly employed. And it is unique, too, in the almost complete control of its manufacturing department by men of scientific college training. A brief survey of the personnel of the Company is extremely illuminating and is one complete answer to the problem of the relation of the scientific man to industry. Of the men I am about to enumerate, the majority hold a doctor's degree, and, those who do not, have had undergraduate training of an extremely thorough character in science or have the training of engineers.

The scientists in the Indiana Company include the president, another director, the general manager of western plants and his assistant, the superintendent, assistant superintendent, refinery superintendent, paraffin works superintendent, assistant superintendent of acid works, and head chemists, all of Whiting, the head of the department of service to licensees, in addition to the usual corps of research men in the laboratory. With such an organization no problem in applied chemistry seems difficult. There is scarcely a man on the manufacturing staff who is not personally capable of solving any ordinary chemical problem, of clearly understanding and passing judgment on any chemical processes submitted, or of putting any ordinary chemical process into practical operation.

Dr. Burton must be given the credit for evolving this system and developing this organization. He has proved by the acid test of practice that the scientifically trained chemist is not only a good theorist but nine times out of ten a first-class executive, and that as an executive he is supremely successful, because of the accuracy with which he can predict results and the speed and directness with which he attains them. This work of Dr. Burton ranks high in importance beside the creation of the process which bears his name.

* * *

In extending to William M. Burton this highest honor in your power, you honor one who has brought honor and credit to your profession, a scientist of scholarly ideals and high attainments, an organizer of broad vision and confident faith in the future, an efficient and successful executive and, perhaps, greatest of all, a leader of men. Dr. Burton asks nothing of his men which he is not capable of doing himself. His greatest tribute, greater far than any award for scientific attainments, is the affectionate regard of those with whom he has worked for so many years and who know him best. Our greatest rewards are not degrees or diplomas, medals or decorations, but the esteem and affection of our associates. These Dr. Burton has long had in abundant measure.

But in honoring him you celebrate a great achievement of your own great profession. May this be only one of a host of like achievements which you have reason to recognize. May these awards, from year to year, mark equally great gifts to human knowledge and human comfort. The day of the chemist is here. You hold the future of industry.

Address of Acceptance

By William M. Burton

The work done under my direction which has perhaps attracted the most attention was carried on principally in the laboratory and refinery of the Standard Oil Company at Whiting, Indiana, and consisted in devising ways and means for the practical conversion of high-boiling fractions of petroleum into low-boiling fractions in such a way as to insure substantial yields of suitable products with a minimum loss and at a reasonable expense.

The problem became imperative with the advent of the internal combustion engine about fifteen years ago. The most commonly known example of such an engine is, of course, the automobile which, as constructed to-day, requires a fuel that evaporates at comparatively low temperatures, has a high heat value expressed in British thermal units, burns without leaving objectionable residues, does not possess an objectionable odor, is low priced, and can be produced in large quantities. Benzene, toluene, and alcohol are fairly well suited for the purpose, but their cost and their small volume of production render them largely unavailable.

The low-boiling fractions of petroleum naturally come into use for this purpose and up to about 1910 the supply of this fuel was sufficient to meet the demand. In fact, the automobile provided an outlet for the sale of these products which, to some extent, had been a drug on the market in the oil world. The older refiners in the country will remember when these so-called naphtha products were thrown away and allowed to run down the streams adjacent to the refineries, thereby causing a wilful waste and a fire menace to the surrounding neighborhood.

Prior to 1910 the average yield of naphtha or gasoline products from crude oil in the United States was about eleven per cent, this yield representing only the amount of such products (of the quality desired at that time) normally present in the crude petroleum, their separation being secured by ordinary methods of distillation at atmospheric pressure; and, further, this small yield was sufficient to furnish all that was needed for gasoline stoves and other industrial purposes prior to the advent of the internal combustion engine for transportation purposes.

When the automobile came into general use, however, it was perfectly clear that the normal yield of naphtha products suitable for fuel in self-propelled vehicles would not be nearly enough. At that time our refineries were selling about forty per cent of the products of crude oil for use as fuel and for gas-making purposes in lieu of coal. The remaining sixty per cent represented the normal yield of naphtha and gasoline, illuminating and lubricating oils.

The above-mentioned forty per cent fuel and gas oil comprised fractions boiling between 225° and 375° C. These oils could, if necessary, be withdrawn from the market, and our problem was to convert them so far as possible into fractions boiling between 40° and 200° C., the product to be equal in quality to normal naphtha products and the yield and operating expense to be commercially practicable.

EARLY EXPERIMENTS

Our first experiments were directed toward making a suitable product by superheating the high-boiling vapors as such, but without pressure, somewhat along the practice observed in making Pintsch gas. We soon found, however, that this so-called "cracking" in the vapor phase required a temperature so high that the aliphatic hydrocarbons contained in the petroleum were largely converted into cyclic and aromatic bodies and fixed gases, unsuited for our purpose. The yield was poor and the quality most undesirable. Obviously our problem included the proposition of reducing the molecular weight without changing the general structure.

We next tried the use of various reagents and catalyzers, such as aluminium chloride and ferric oxide. Anhydrous aluminium chloride, indeed, produced some rather remarkable results. The yield and quality of naphtha products were fairly satisfactory but there was a substantial loss of oil in the operations, and the first cost of the anhydrous aluminium chloride, as well as the difficulty in recovering it from the residues, rendered this plan unattractive.

Nearly thirty years ago Sir Boverton Redwood and Professor Dewar in England patented a pressure distilling process for the purpose of increasing the yield of kerosene oil from the residues of Russian crude petroleum, but it never was applied industrially. It has been known, therefore, for some years that distilling petroleum under pressure served to break down the high-boiling fractions into low-boiling fractions but, as far as we could learn, no one had ever done it on the large scale and, in fact, such a proposition could not commend itself to a practical refiner because of the obvious dangers from explosions and fires.

But having tried everything else that suggested itself, we attacked the problem of distilling petroleum in considerable quantities (8000 to 12,000 gallons) under pressure of about five atmospheres. Our first still was of a welded design and was planned to handle 100 gallons of the high-boiling fractions. Obviously, the raw material first to be tried consisted of the so-called fuel oil, or reduced crude, meaning the residue of crude oil after the more valuable products had been removed. We soon found that we could not work profitably with this product; when distilled with or without pressure it produced quantities of coke that deposited on the bottom of the still and caused a red-hot bottom that would not stand any rise in pressure. The next proposition comprised the use of high-boiling distillates from the crude, *viz.*, oils boiling from 225° C. upwards. We distilled these distillates at a pressure of about five atmospheres and were thereby able to hold down the temperature to a moderate figure, the cracking being done in the so-called liquid phase. We found to our intense gratification that the low-boiling fractions produced belonged mostly to the paraffin series, which were easily deodorized and finished into products suitable for sale. Further, the yield of salable liquid was good and the production of fixed gases and coke was small.

LARGE-SCALE DEVELOPMENT

Experimentally, therefore, our work was successful. But the big problem remained to be solved. Could we build large equipment that would, in a practical way, secure the desired results and at the same time be durable and reasonably free from the fire hazard that always attends operations in an oil refinery? Some of our practical men said we could, but more of them said we couldn't. In this case, however, the majority was overruled and we immediately prepared plans and specifications for a still eight feet in diameter and twenty feet long, built of one-half inch mild steel plate, which would charge 6000 gallons of raw material. It had a safety factor of 5, the working pressure to be 100 pounds and the bursting pressure 500 pounds.

The still was built and charged, with many misgivings on the part of the doubters, but with boldness and confidence exhibited by the rest of us. So soon as we had the still hot and pressure began to develop, we encountered our first difficulty. The still was built in a workmanlike manner and would have made a good steam boiler, but rivets and seams leaked badly under oil pressure where they would not under steam pressure. It was difficult to induce boilermakers to calk the leaks while the still was hot and under pressure, but we found men bold enough to do it, and the first run was sufficiently encouraging to induce us to proceed further. But the leaks persisted until Nature came to our aid and the minute portions of oil in the leaks gradually carbonized, they closed without our aid.

The experiments with the large still proved our results with the small one, *viz.*, the yield of suitable gasoline fractions was good; the loss was trifling; the cost was reasonable, and the fire hazard under close caution and supervision was not excessive. Further, we were astonished to find that the residue remaining in the still contained substantial quantities of asphaltine actually created (from a distillate containing none of it) by distillation under pressure.

We learned early in the work that operating at moderate pressure required a substantial dephlegmating system that would return to the still fractions boiling too high for our purpose, and allow the others to pass on.

A suitable safety valve that would operate properly with oil vapors at high temperature had to be devised. After making a number of runs with our 8 × 20 still, and in view of the fact that the demand for gasoline was increasing at a rapid rate, we asked for an appropriation of one million dollars to build sixty pressure stills eight feet in diameter and thirty feet long, each charging 8000 gallons of raw material. Considerable argument was required to convince any of our directors that such a revolutionary proposition could possibly be successful, but finally they voted in favor of it, and we went ahead.

It would require much more time than I have at my disposal this evening to give a full account of the minor difficulties that arose. We had solved the big points, but there were many smaller ones. For successful results we must operate with the oil at temperatures from 370° to 400° C. in the still. At 450° C. steel begins to lose its tensile strength and its capacity to withstand pressure. It is clear, therefore, that with this narrow margin great caution must be exercised to prevent overheating. The human element enters here, as it does in every feature of pressure-still operation, but we operated over eight years with hundreds of these stills in daily use, and manufactured millions of barrels of gasoline by this method before we had a fatal accident.

THE PRESSURE-STILL INDUSTRY TO-DAY

From the humble beginning of the 100-gallon still in our experimental laboratory, the Standard Oil Company of Indiana has in operation to-day over eight hundred pressure stills having a gross charging capacity of eight million gallons, and licensees under our patents are operating as many more, giving a daily production of two million gallons of gasoline out of about twelve and a half million gallons total daily output in the United States and Canada.

This amount of gasoline makes possible the use of two millions of motor vehicles more than could otherwise have been supplied from a given consumption of crude petroleum, and as a corollary of that proposition, and assuming 20 per cent of gasoline as a normal average yield from crude oil, the pressure-still process is conserving for future consumption an amount of crude oil nearly equal to one hundred million barrels per year.

The consumption of gasoline by internal combustion engines during the past decade has increased at a terrific rate. In 1910 the United States consumed approximately seven hundred million gallons, while for 1920 the Bureau of Mines statistics show a total gasoline production of four billion six hundred million gallons, of which eight hundred and fifty millions were made from natural gas, something over three billion gallons made by straight crude oil distillation, and seven hundred and fifty million gallons made by the cracking process. Further, statistics show that while the increase in crude oil production during the past decade has been one hundred and forty-two per cent, the increase in gasoline production has been over seven hundred per cent, and although some of this gasoline has been exported, the larger portion has been consumed by the ever-increasing number of automotive vehicles in this country.

The increase in production of crude oil has not been commensurate with the increased demand for its products, and the pressure-still process has filled at least part of the gap. Naturally, one is inclined to speculate on what the future will be regarding an adequate supply of these important commodities. One suggestion would be that some of the large amounts of oil now being used for fuel and gas-making purposes be replaced with coal, and substantial portions of the oil used for making gasoline, the coal consumption, in turn, to be replaced in part by the further development of hydroelectric power.

The American people are notoriously wasteful in the use of natural resources with which they are so richly endowed. It is hoped the work outlined above will be considered a slight contribution toward the curtailment of such waste.

It would be obviously unfair and unjust to close this paper without duly acknowledging the work done by my associates in successfully establishing the pressure-still process. Our patent attorneys, represented by Mr. Russell Wiles, contributed many useful and practical suggestions, and if it had not been for the invaluable assistance of Dr. R. E. Humphreys, Mr. E. M. Clark, Mr. T. S. Cooke, and many others connected with the Standard Oil Company of Indiana, satisfactory results would never have been secured.

A new color card showing dyes for cotton has been issued by the National Aniline & Chemical Co., Inc., which embodies several new and useful features. For the first time there has been produced a table of dyeings and tabulations explaining the fastness properties of each one of the dyes included, with the information given in easily understood language instead of being indexed and indicated by numerals. The tabulations explain such conditions as fastness to washing, light, acid, alkali, and hot pressing, as well as hydrosulfite discharge properties. General directions for the use of these dyes for cotton are also given.

Pfanstiehl rare sugars and amino acids, to the development of which the Special Chemicals Company of Highland Park, Ill., has given special attention, are now used by investigators around the world, from China and Japan, through every land in the new world, to Ireland, England, Denmark, France, and now to Germany. Because of their purity they have become a world standard and to America's credit it can now be said that another important contribution has been made to scientific accuracy and precision by means of materials of a new standard embodying the latest requirements of bacteriology.

A vocational course in papermaking has been started at Woronoco, Mass., under the auspices of the Strathmore Paper Company. The purpose of the course is to give a technical as well as a practical knowledge of the work in which the men are engaged. Under the present plans the company will pay for the various courses, charging small fees to students, and refunding the fees to all those who have passed a certain standard.

NOTES AND CORRESPONDENCE

A Foreign Opinion of the American Chemical Society

Editor of the Journal of Industrial and Engineering Chemistry:

Dr. Herty in his last editorial, and in his genial way, gave us a short sketch of the work accomplished by the American Chemical Society during these latter years.

May I call your attention to the published opinion of our distinguished fellow chemists in France and in Britain. From that excellent French publication, *Chimie et Industrie*, **6** (October 1921), 418, I make the following free translation of a report of the annual meeting of the Société de Chimie Industrielle:

> Among the ideas presented by pen or word during this convention, there is one which seems of foremost importance for our country. It was expressed by Sir William Pope, to whom our Society has just awarded its Grand Medal of Honor, when he made the following statement in the presence of the Minister of Agriculture:
>
> *The American Chemical Society with its 17,000 members represents collectively all the interests of American Chemistry. On this account, it has become, in a way, the diplomatic corps of Chemistry in the United States, and every time the government has before itself questions where chemistry enters into play, senators and politicians immediately ask information and advice from the American Chemical Society.*
>
> If ever the Société de Chimie Industrielle of France saw itself honored as such an authority, what valuable services would our country obtain thereby!

Of course we all know that our politicians are not so ever ready to consult the American Chemical Society, but it is undeniable that since the growth and importance of our Society, its advice and opinion have frequently guided the Government and the better of our politicians.

L. H. Baekeland

Yonkers, N. Y.
December 3, 1921

The Chemical Industries of Holland

Editor of the Journal of Industrial and Engineering Chemistry:

As a chemist subscriber of *The Journal of Industrial and Engineering Chemistry*, I read the article on the "Chemical Industry and Trade of Holland" in your July number with much interest.

Generally speaking, your correspondent has very well represented the leading points, but I should greatly appreciate it if you would rectify or add a few points.

Under the heading of "Dyestuffs," it is said that the production thereof is insignificant and will probably remain so unless the Germans find it advisable to have plants in Holland. Your correspondent is probably not aware of the fact that, apart from a few smaller works which produced dyes even during the war, a company was founded about a year ago with the purpose of taking up the production of dyes with purely Dutch capital. This is the N. V. Nederlandsche Kleurstoffenfabriek (Dutch Dyestuffs Factory). The large banking houses, such as the well-known Twentsche Bank, Messrs. Mees & Co., large industrial concerns, such as the Bataafsche Petroleum Co., and other leading firms have all given money for establishing this national industry.

Further, your correspondent does not touch upon the large sugar factories which we have here in Holland. A large part of colonial sugar is refined here, and we have also some twenty beet-sugar factories. A fair amount of concentration has been effected of late in this industry, many beet-sugar factories having combined with the largest refining company under the name of "Centrale Suiker Maatschappy." It is very interesting to see that this concentration has taken place although the tendency of the sugarmaking process is undoubtedly to make white sugar under the same roof with the beet sugar, so that each beet-sugar factory would make its own white sugar and not send its raw sugar to a refinery. The largest refinery here, probably having foreseen this, secured the necessary beet-sugar factories in the above-named company.

E. J. Tobi

Ceintuurbaan 213
Amsterdam, Holland
August 24, 1921

Ceramic Research Colloquium

Held November 16 and 17, 1921, Ohio State University, Columbus, Ohio, under auspices of American Ceramic Society Committee on Research and Development, Central Ohio Local Section and Ohio State University Student Branch of the Society.

The Committee on Research devoted all day Wednesday and Thursday forenoon to the general question of policies and procedures most practical for stimulating ceramic research.

Research can be defined as systematic search for best ways and means of accomplishing some definite thing. A thoughtful study of and practice in best methods of accounting, marketing, etc., is research. Diligent thinking, experimenting and inventing of materials, mixtures, processes, and equipment for producing ceramic wares is ceramic research. It is only in these latter research problems that the Society is interested.

The American Ceramic Society was founded for and has continued to be engaged in the promotion of the ceramic arts and sciences through stimulation of research by individuals, corporations, governmental departments, universities, and associations of manufacturers. Holding of meetings for open discussions; planning by committees for unity in efforts; encouraging and assisting in coöperative efforts to ascertain facts relating to manufacturing; publication of literature, are examples of the means employed by the Society to promote ceramic arts and sciences through research.

The Society is divided into industrial divisions for the purpose of having more intimate contact with and knowledge of manufacturing problems. The divisional committees on research are requested to submit a list of research problems with a description of each item, suggestions as to where the problems might be undertaken and such suggestions and recommendations as they care to make. These lists will be studied and a grand program of activities planned, which program will again be submitted to the divisions for amendment or adoption. Some of the divisions already have such a list and have proceeded in interesting universities, governmental departments and associations.

One of the contacts sought by the Research Committee is that of the users of ceramic products. It is necessary, for instance, to understand the requirements of boiler refractories in order to know how to manufacture bricks for this purpose. The American Ceramic Society offers the best opportunity for the producers and users to meet in joint effort to solve the problems of the consumers.

A well-rounded sales promotion plan includes detail study of consumers' requirements. Sales promotion without this would not be successful. This is equally true in ceramic research. The interest of the consumer, which has for the most part been neglected in the past, will now receive adequate attention by the ceramists through the agency of the research committees of the Society and the divisions.

Actual contact will be had with the members of the Society and with the public at large through the issuance of bulletins. No opportunity will be neglected to make the researches conducted under the auspices of the Society as thoroughly practical and far-reaching as is humanly possible. Fundamental science investigations are just as practical and necessary as are factory or routine investigations. Neither should or will be neglected. Industrial corporations and research institutions will be consulted for the purpose of finding not only the problems but also the means for solving them.

Standard methods and specifications have not in the past received the attention they deserve. The Society intends to promote the establishing of standards by securing the coöperation of all parties and agencies interested. The Society has joined as a member of the American Society for Testing Materials, and will have an official representation on all committees where the Society can give service. It is coöperating with all Divisions of the National Research Council that deal with problems of interest to ceramists. A working relation has already been established with the Fabricated Production Department of the Chamber of Commerce of the U. S. of America. The trade associations recognize the desire of the American Ceramic Society to coöperate with them in all matters of standards and researches pertaining to production. Contact is developing with the federal and state Geological Surveys, so that the Society can serve the Surveys in making their investigations the most practical.

This research colloquium was not devoted altogether to planning. Some research problems were discussed in detail.

At the public meetings of the colloquium, those attending obtained a much more clear and practical idea of the cause of plasticity in clays. The ultimate purpose for searching for the facts regarding plasticity is that this property may be developed in the white-burning kaolins. Ceramists have obtained several practical and applicable things from the studies which have already been made on this subject. The treatment of casting slips with salts to make possible the casting of intricate and heavy pieces is one of these, and increasing the bonding strength of clays is another.

More refined methods of testing were discussed. Dr. E. W. Washburn described a method developed at the University of Illinois for measuring porosity by determining the pressure caused by the air held in the pores of the test piece. The method he described is simple, accurate, and quick.

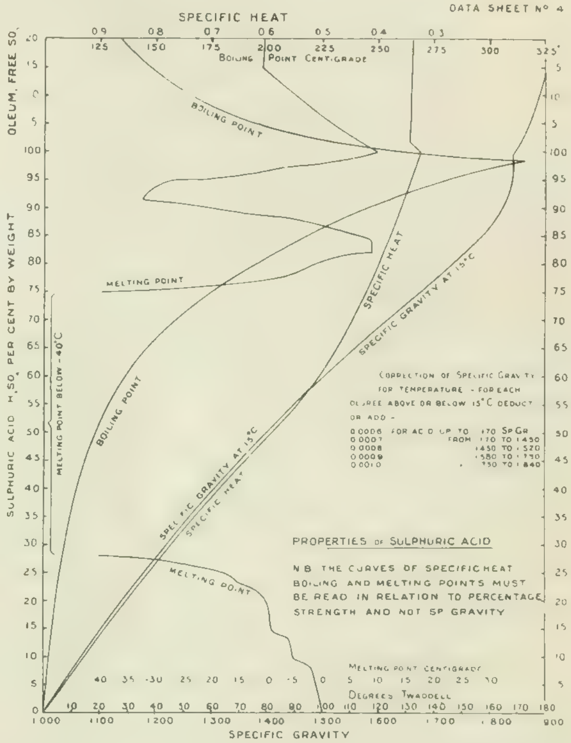
President Pence described the problems incident to casting of clay refractories. The method he described produces better ware but requires considerable floor space if the production is at all large. In a 50 per cent grog clay refractory 0.4 per cent of the weight of clay added as sodium carbonate would permit of the same degree of fluidity of the slip with one-half the amount of water.

The U. S. Bureau of Mines, with consent of the Joint Research Committee of the Four Heavy Clay Products Associations, described the work on kiln firing which the Associations are financing in coöperation with the Bureau. This work is progressing and when other groups of manufacturers learn of the results obtained it would seem that surely all ceramic manufacturers would be anxious to make a similar study of their kilns. A 10 to 15 per cent saving in fuel would soon pay all costs of the preliminary studies and all the equipment required to maintain the necessary control. We are learning that scientific control in manufacturing reduces costs and decreases dependence on experts. No research is worth while unless it carries through to the introduction of materials, processes or equipment, alike satisfactory to employees and employer in the control obtained.

It is believed that this meeting is only the first in the series of events which will bring a new era in ceramic manufacturing and keep this group of industries abreast with the ever-increasing requirements of the consumer.

Chemical Engineering Group of the Society of Chemical Industry

The Chemical Engineering Group of the Society of Chemical Industry is the first of what have been termed "Subject Groups" of the Society, corresponding in a general way to the Divisions and Sections of our American Chemical Society. It was organized in 1919 by a group of chemical engineers who felt the need of an organization in England, charged with the task of endeavoring to promote the interests of chemical engineering and its development along sound and scientific lines.



Among the activities of the Group is the publication of data sheets and charts, one of which is printed herewith in greatly reduced form. These sheets cover a large field of interest to the chemical engineer, and it is planned to publish a whole series, uniform in size, for filing in loose-leaf books. The sheets are sold at fifty cents per set. Membership in the Group includes the receipt of its publications. The headquarters of the Group are at 24, Buckingham Street, Strand, London, W. C. 2, England.

Calendar of Meetings

American Institute of Mining and Metallurgical Engineers—Spring Meeting, New York, N. Y., week of February 20, 1922

American Ceramic Society—24th Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922.

American Chemical Society—63rd Meeting, Birmingham, Ala., April 4 to 7, 1922.

American Electrochemical Society—41st Meeting, Baltimore, Md., April 27 to 29, 1922.

A German process for making gasoline, called the Burgess process, has been developed by the originators of the Haber nitrogen fixation process. By means of this process, hydrogen is passed over carbon at 200 atmospheres pressure and at a temperature of 700° C. It is understood that this process has been examined in operation by the engineer of one of the large American oil companies who has reported that it is actually operating and producing motor fuel on a small scale.

WASHINGTON NOTES

Hearings on Potash

Opposition to protection of the American potash industry developing in the Senate Finance Committee hearings on December 29 was limited to five obstructionists: one a fertilizer man interested in German mines; one a representative of those interests; one alleged farmer's friend who claimed that one of the Central States used more potash than any other state in the Union; a professor who stressed a possible increased cost of 2 cents per bushel on potatoes; and a practical farmer who admitted that the lack of an American potash industry at the beginning of the war was disastrous to his agricultural interests and announced his desire for the firm establishment of a domestic potash industry.

The American producers had their day on December 30, their spokesman, Mr. LaRoe, attorney for the United States Potash Producers' Association, urging an annually diminishing protective tariff consisting of 50 cents per unit for two years, 40 cents the third year, 30 cents the fourth, and 20 cents the fifth year. The proponents of the bill emphasized the industry's very recent birth in the United States and its dire need for protection for about 5 years, which would enable it fully to meet Germany in the open market.

It was shown that the tariff would add not over 25 cents per acre to the cotton planters' costs or two-tenths of 1 cent a pound to tobacco producers' costs. The claims of the opponents of the industry to America's alleged limitations were refuted by statistics presented showing authoritatively that there are in Searles Lake, Cal., 20,000,000 tons of potash, equal to normal domestic needs for 100 years; in Nebraska 3000 deposits of from 1 to 600 acres each; in one Wyoming County 200,000,000 tons of leucite rock of 11 per cent pure potash content, or an 800 years' supply. It was pointed out that the war-time potash production costs of $4.50 or $4.25 have fallen to about $1 per unit, with an additional reduction in sight if the protection sought is granted. American producers have available about 10,000 tons of K_2O and are ready greatly to expand and improve their plants, with a resultant decreased cost to the consumer, within 5 years, if the bill is enacted. It was urged that with the country's abundant potential potash resources, with existing plants capable of producing 75,000 tons of K_2O annually, and with $30,000,000 invested, Congress had more than ample reason for not permitting this young American industry to die for lack of protection by the United States Government.

House Passes Bill to Relieve Patent Office Situation

A ray of hope appears on the horizon for the overburdened Patent Office in that the House has finally passed the Lampert bill to increase the salaries of the chief or principal patent examiners from $2700 to $3900 per year and those of the assistant examiners by amounts ranging from $150 to $900 per year. The bill provides an increase of force to the extent of one law examiner, 26 assistant examiners, and 22 clerks. While this bill is by no means adequate to relieve the present difficult position of the Patent Office, it is at least a step in the right direction, and it is hoped that the Senate will lose no time in acting upon the measure.

Possibility of Buried Potash Salts in Western Texas

In connection with borings for oil which are being made by the U. S. Geological Survey in the extreme western part of Texas, salts have been discovered that apparently possess at least the richness of the potash deposits of Alsace and Germany. Polyhalite, hydrated calcium potassium magnesium sulfate, has been found in a number of different levels in these borings, but as the wells are being drilled primarily for oils, information is not at present available as to whether the potash-bearing beds have a thickness of only a few inches or a much greater depth. The polyhalite examined contained 15.6 per cent of K_2O and it is believed that it can be used as a fertilizer in the pure state in which it is recovered, provided it is found in sufficient quantity.

Bureau of Mines Laboratory Car

In the coöperative work which is being conducted at the Columbus Station of the Bureau of Mines with the four heavy clay products associations, a laboratory car has recently been purchased. This is the first laboratory car that the Bureau has equipped and is similar to the Bureau's rescue cars. It is known as the "Car Holmes" in honor of the first director of the Bureau, and is a Pullman with living accommodations, laboratories, and office facilities for use at all hours. The investigation crew will visit various industrial plants with a threefold purpose: to cut down fuel consumption; shorten the time of burning; and improve the quality of the product. The first trip was made from Columbus to one of the hollow tile plants of the National Fireproofing Company at Haddonville, Ohio.

Furfural Production and Utilization

In connection with the research work of the Bureau of Chemistry on the production and utilization of furfural, a small experimental plant has been installed at the Color Laboratory, Arlington Farms, Va., with a capacity of 30 lbs. per day. Corncobs digested with high pressure steam yield furfural equal to 6 or 7 per cent by weight of the cobs. The yield obtainable from other agricultural wastes will be investigated.

Over 300 lbs. of furfural have been manufactured in connection with production experiments at the Bureau of Chemistry during the past year. The greater part of this material has been supplied to several manufacturers for coöperative work on commercial utilization. The most promising field yet developed by this coöperation is that for the production of synthetic resins by the condensation of furfural with phenol. These resins have qualities suitable for electrical insulators and other molded articles which are being tested commercially.

Lack of Funds Delays Establishment of Chemical Division

The Bureau of Foreign and Domestic Commerce is finding it difficult to secure funds to organize a Chemical Division. Estimates have been submitted to Congress for the establishment not of one chemical division, as originally planned, but of three such divisions—one on heavy chemicals, one on dyes and drugs, and still another on paints and varnishes. If these divisions are organized a live contact will be maintained with the trade through the formation of an advisory committee in the industry itself, and whenever acute problems arise in foreign districts it will be the duty of a representative of the Bureau to travel to such points and assist in relieving the situation.

Under an informal agreement entered into between the Bureau of Mines and the Department of Geology, Indiana University, investigations of Indiana oil shales are now being conducted at the Indiana University under the direction of the Bureau of Mines.

The plans of the new building for coöperative laboratories of the Bureau of Mines and the University of Minnesota at Minneapolis have been completed and approved, the cost of construction being estimated as $250,000, the funds for which are contributed by the State of Minnesota. The building will not be ready for occupancy in less than a year.

The demand for industrial alcohol has grown to such an extent that at the present time there are 58 formulas employed for its preparation. To meet the needs of both the manufacturer and the user, the Industrial Alcohol and Chemical Division of the Treasury Department, in coöperation with the Bureau of Standards, is at present engaged in the preparation of tables of specific gravities and weights per gallon of these various formulas. These tables will later appear as a government publication.

The Tariff Commission has in preparation for the Senate Committee on Finance a revision of the Summary of Tariff Information, 1920. This compilation will include statistics and other information for the first nine months of 1921.

The Tariff Commission is also compiling a digest of the hearings before the Senate Finance Committee.

The Bureau of Mines plans to engage an engineer who will be stationed at Reno, Nevada, to carry on nonmetallic investigations throughout the West.

A study is being made by the Bureau of Mines of the unsaturated hydrocarbons in industrial gases with a view to developing economic methods for the manufacture of alcohols therefrom. Ethyl and propyl alcohols are being sought particularly. Gas distilled from a mixture of oil and coal is at present being studied in coöperation with the Trent Process Corporation, of Washington, D. C.

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Although the question of naval disarmament, coupled with the Pacific question, seems to occupy a leading place at the Conference in Washington, one cannot neglect the matter of land disarmament, from the particular point of view which appeals to us chemists.

There has just been organized in Germany a Union for the defense of the interests of the German chemical industries. One of the first manifestations of the Union has been a complaint of the wasting away of chemical industry in Germany. It is evident that all the allied and neutral nations which were clients of Germany before the war have had to establish their own chemical industries. There has resulted at the present time a world over-production of chemicals, and Germany, who even in 1920 held second place in export of chemical products, finds her exports, and consequently her production, reduced in 1921 to 50 per cent of what it was in 1914. Further, the German chemical industry blames the import tariffs for this paralysis. Formerly, many German chemical products were exported to Switzerland, from which they were finally shipped to the various consumers. Exports to Switzerland in 1920 were 290 million marks, of which about half were chemicals, but Switzerland has just quadrupled her import duty, thus practically stopping the export of German products. Under these conditions, and in spite of the fact that the low value of the mark should at the moment aid the German chemical industry, the complaints of the directors of this industry, who go so far as to say that Germany cannot meet her obligations to the Allies on account of this economic situation, are explicable. These arguments might have some weight, did one not feel a back thrust at Mr. Francis Garvan and Dr. Herty, as well as at Mr. Victor Lefebure, gas officer in the British army. The last mentioned is at present conducting a campaign in England in which he is demanding severe control of German chemical factories, from the point of view of gas manufacture; it is this control which the Germans wish to avoid at any cost.

The Fuel Situation

I have already mentioned several times a contest for a national fuel, with the object of finding a better formula for a motor fuel containing alcohol.

Mr. Marillier has just reported to the Académie des Sciences the solution of the problem. Absolute alcohol is miscible with gasoline, but 95 per cent commercial alcohol is not miscible. When 95 per cent alcohol is mixed with gasoline two layers are formed, and on account of the partition factor the water in the alcohol is almost entirely in the lower layer, while the upper layer contains gasoline with 10 per cent of anhydrous alcohol. This layer serves as a basis for the fuel, to which it is sufficient to add small quantities of benzene, methylene, and ether.

I have also frequently noted the prospecting for petroleum in various parts of France. At present, the boring at Vaux (Ain) is becoming industrially important. Three test borings were made in 1920 and the beginning of 1921. A fourth boring, ended in October, is yielding now steadily 90,000 cubic meters per day. The gas is to be used for lighting the town of Amberieu. It contains 80 per cent of methane, 12 per cent of different hydrocarbons, higher homologs, the remainder consisting of nitrogen, carbon dioxide, and carbon monoxide. The calorific power is 9500 calories.

Carbonization of Coal

In the same field I have mentioned the recent discoveries of Mr. Charpy on the carbonization of coal.

This problem has found a special application in the case of the Sarre coals, which give a coke too friable for use in the large blast furnaces. Mr. Charpy has studied carefully the conditions of the oxidation of the coal, and the mixtures of fat and lean coals. He has arrived at the conclusion that to obtain a good metallurgical coke it is necessary, in addition to making a judicious mixture of the coal, to conduct the carbonization in two stages. In the first step, the coal must be raised instantly to a temperature of 450° to 500°; then, in the second step, the temperature must be raised extremely slowly to between 700° and 900°. These theoretical considerations have been tested out industrially in the basin of the Sarre, with good results.

1922 Meeting of the Société

The success of the meeting of the Société de Chimie Industrielle last October has led to plans for the 1922 meeting, which will be held in Marseilles, July 2 to 6. It will cover principally the chemistry of fats and the chemistry of vegetable products from the colonies. The meeting will take place at the same time as the interallied colonial exposition.

December 10, 1921

I have just met Professor Moureu as he was returning to his laboratory at the Collège de France. He gave me his impressions on his sojourn in the United States and recounted the unforgettable welcome he received. Naturally, Professor Moureu is very discreet in regard to the work of the Conference, but he told me enthusiastically of the reception which he received in various chemical fields, official, university, and industrial. He believes that the United States is making a great advance in chemical research and in the creation of a great industry, mineral as well as organic. This industry will be the most powerful in the world and, with the high idealism of the American people, it will be a guarantee of peace. For us Frenchmen it constitutes one of the best elements of our security.

January 6, 1922

PERSONALS

Mr. Ernest H. Hartwig resigned as assistant in chemistry at Purdue University in order to accept a position as instructor in the chemical engineering department at the University of Wisconsin, Madison, Wis.

Miss Henriette C. Liebe recently received her B.S. degree from the University of Wisconsin and has accepted a position with the Acme White Lead and Color Works of Detroit, Mich., where she is an executive research chemist in the research division.

Mr. Raymond L. Stehle recently resigned as assistant professor of physiological chemistry in the School of Medicine of the University of Pennsylvania to become associated with the faculty of medicine of McGill University, Montreal, as assistant professor of pharmacology.

Mr. Merrill C. Hart, who was chemist to the pharmacology department of the University of Minnesota, working on the synthesis of phenolic alcohols on funds granted by the U. S. Interdepartmental Board for Social Hygiene, is associated with the Upjohn Company at Kalamazoo, Mich., as research organic chemist.

Mr. W. H. Rodebush has been appointed associate professor in charge of the division of physical chemistry, University of Illinois, Urbana, Ill. Mr. Rodebush was formerly national research fellow at the University of California.

Mr. Harvey T. Kennedy, formerly a student in chemistry at Cornell University, Ithaca, N. Y., has become chemist in the Municipal Testing Laboratory, Rochester, N. Y.

Mr. James H. Ransom has changed his position as research chemist with the Michigan Smelting & Refining Co., Detroit, Mich., to head of the department of chemistry in James Millikin University, Decatur, Ill.

Mr. Gerhard K. Rollefson resigned as assistant in chemistry at the University of Wisconsin to accept a position as teaching fellow in chemistry at the University of California, Berkeley, Cal.

Mr. F. Arthur Patty, instructor in chemistry and pharmacy at the University of Washington, Seattle, Wash., accepted his present position last August with the Campbell System, Inc., Kansas City, Mo., as research chemist.

Mr. John C. Pennie, for many years a specialist in the practice of patent law, died at his home in New York City on December 23, 1921. Mr. Pennie was born in Albany, N. Y., in 1858. He graduated from Union College in 1877, and pursued postgraduate work in Germany at the Universities of Göttingen and Heidelberg. He entered the United States Patent Office as an examiner in 1880. He practiced patent law in Washington and New York and at the time of his death was a senior partner of the firm of Pennie, Davis, Marvin and Edmonds.

He was chosen by the United States Government as patent expert on the commission to negotiate peace, and spent six months in Paris advising with the representatives of other countries on the provisions of the Peace Treaty relating to patents. He was a member of most of the learned and scientific societies, of the Legion of Honor of France, and Commander of the Order of the Crown of Belgium.

Dr. William Frear died suddenly at his home at State College, Pa., January 6, 1922. Dr. Frear was born in Reading, Pa., March 24, 1860. He received the bachelor's degree from Bucknell University in 1881, and the doctor's degree from Illinois Wesleyan University in 1883. After two years as an assistant chemist in the U. S. Department of Agriculture, Dr. Frear became associated with the agricultural department of Pennsylvania State University, and had been director of the Experiment Station since 1887.

Following the lines of Dr. Smith's suggestions to members of the Society in regard to popular education as to chemistry, **Dr. C. E. Kenneth Mees,** director of the Research Laboratory of the Eastman Kodak Co., addressed the Rochester City Club on January 7 on the importance of scientific knowledge and its application to life.

Mr. Daniel H. Rupp, formerly chemist for the Clark-Parker Chemical Co., Los Angeles, Cal., and later with the U. S. Potash Co., at their Monolith cement plant, is at present connected with the City of Ironton, Ohio, as "chemist-in-charge" of water purification works.

Dr. Lansing S. Wells, until recently research chemist with The Barrett Company, Frankford, Philadelphia, Pa., has accepted an appointment as assistant professor of organic and physical chemistry, Montana State College, Bozeman, Mont.

Dr. R. L. High, for fifteen years chief chemist to the National Drug Company of Philadelphia, Pa., recently resigned his position in this capacity and opened the High Chemical Company at Savannah, Ga.

Mr. Donald Belcher is now employed by Perin and Marshall, consulting engineers, of New York City, as a chemical engineer on development work for a process which he worked on as a research chemist for Hayward and Schleicher, of Cambridge, Mass.

Mr. Louis J. Trostel, who for the past two years has been stationed at the Pittsburgh Station of the Bureau of Mines engaged on problems relating to industrial gases and dusts, resigned November 1 to take a position with the Bureau of Chemistry as assistant chemical engineer. He will there be associated with the work of the Bureau on chemical problems relating to explosions from starch and other carbonaceous dusts.

Dr. Raymond J. Miller, formerly with the department of physiological chemistry, Jefferson Medical College, Philadelphia, Pa., as research associate under Prof. Philip B. Hawk, is at present associate professor of pharmacology and physiological chemistry at Baylor University, College of Medicine, Dallas, Texas.

Dr. Minnie A. Graham, who has served as substitute for Prof. Charles J. Moore of the department of chemistry of Hunter College of the City of New York, has been appointed acting professor of chemistry at Wells College during the absence of Prof. Clara A. Bliss.

Mr. Arthur W. Davidson, who was library investigator at the library of the Chemists' Club from last February to August, has been appointed assistant professor of chemistry at the University of Kansas, Lawrence, Kans.

Mr. A. E. Marshall has resigned as works manager of The Davison Chemical Company and has returned to his former work as consulting chemical engineer, specializing in the design of plants for the manufacture of mineral acids and fertilizers, at Baltimore, Md.

Dr. Ernest Fox Nichols, who recently resigned the presidency of the Massachusetts Institute of Technology, is to return to Cleveland to resume the directorship of pure science in the Nela Research Laboratory of the General Electric Co.

BOOK REVIEWS

Organic Compounds of Mercury. By Frank C. Whitmore. (American Chemical Society Monograph Series.) xii + 397 pp. The Chemical Catalog Co., Inc., New York, 1921. Price, $4.50.

The interest in the study of organic compounds of mercury has increased in recent years because of the need for some non-ionized mercury compound for use with organic arsenicals in the treatment of syphilis. This volume is principally confined to the consideration of true organic mercury compounds in which mercury is directly attached to carbon. The related subjects which are not discussed are made available for further study by the supplementary biographical lists included in the appendices. The author states in the preface that "the monograph will be arranged to serve both the general chemist who wishes to get a conception of what has been done in the field, as a whole, and the specialist who wishes to find out quickly what has been done in any particular field. It is hoped that the work will inspire further research in this interesting field. In general, enough detail is given to make evident the method, but not enough to serve as a laboratory guide in repeating any of the work."

One is impressed with the great variety of mercury compounds, the new methods of preparation, and the improvements in the older methods. Little more seems to be known about the part played by ethyl acetate in the formation of mercury alkyls than was known by Frankland sixty years ago. It is interesting to note that in making alkyl mercury compounds 0.1 per cent sodium amalgam gives the best results, while for the aryl compounds 2.7 per cent sodium amalgam gives the best yields.

The word "mercurate" has been introduced to conform with bromination, nitration, and sulfonation. In fact, it has been shown that mercuration of aromatic compounds follows the general rules of substitution except in the case of nitrobenzene. Mercuration of aromatic compounds with mercuric acetate has led to many new and interesting compounds. The properties of most of these compounds have been studied, but in a number of cases the constitution has not been definitely determined.

The fairest comment that can be made upon this book is that the author has accomplished that which he set out to do, and chemists are indebted to him for this admirable piece of work. Anyone familiar with these very interesting compounds will appreciate the service that he has performed. The book is well planned, well written, and well printed. It will make a valuable addition to any chemical library, and those interested in mercury compounds cannot afford to be without it. It is a real addition to our American chemical literature.

Walter T. Taggart

Animal Proteins. By Hugh Garner Bennett. xiv + 288 pp. D. Van Nostrand Co., New York, 1921. Price, $3.75.

This is another volume of the series of Industrial Chemistry edited by Dr. Samuel Rideal. The title is clearly a misnomer, as the book can lay claim to being little more than a semipopular description of the manufacture of leather and glue. It does not describe, or even enumerate, the several proteins of which skin is composed. The only conceivable justification for the title is that the proteins of leather and glue are of animal origin. Of the six parts into which the book is divided, four are devoted to tanning, one to glue manufacture, and one to by-products, with very brief mention of foods and fertilizers.

It was intended to include in each book of the series a general bibliography and also a selective bibliography to follow each section. In this book there is no general bibliography and the selective bibliography is so meager and inaccurate as to be of little value. The *Collegium* is given as the source of articles which it merely reprinted or abstracted, and apparently no attempt has been made to record titles accurately.

The book will appeal to the layman desiring a general description of leather and glue manufacture and to the practical tanner desiring to know something of processes other than his own. The author's attempt at chemical treatment, however, cannot be regarded as successful. The term *lyotrope* is used very freely throughout the book as though in itself it describes or explains numerous phenomena.

On page 26 we read: "In bating and puering the essential change is that before the process the swelling is due chiefly to adsorption of hydroxyl ions, whereas afterwards it is due chiefly to a composite lyotrope influence." Upon examination, this proves to be nothing more than a jumble of words, but it is typical of the attempts at theoretical treatment. In keeping with the meager bibliography, the author ignores, or is possibly unaware of, much of the literature on the phases of leather chemistry which he attempts to discuss.

As a rule, vegetable leathers are firmer and more solid than chrome leathers. The author explains this as being due to the greater deposition of solid matter on the surfaces of the fibers and in the spaces between them by vegetable than by chrome tanning. He apparently does not know that it has been demonstrated microscopically, in carefully controlled systems of both chrome and vegetable tanning, that there is no visible deposition of tanning material on or between the fibers, but that the tanning material diffuses completely throughout the protein substance, altering its chemical and physical properties. Vegetable tanning causes a much greater solidity by producing a greater increase in volume of the fibers than does chrome tanning. This is easily seen by examining sections of leather under the microscope.

While the book presents little that is new, its general descriptions of numerous methods of making leather will make it welcome as a book of reference in many tannery libraries.

J. A. Wilson

The Metallurgy of the Common Metals. By Leonard S. Austin (formerly professor of metallurgy, Michigan College of Mines). 5th edition, 615 pp., illustrated. John Wiley & Sons, Inc., New York, 1921. Price, $7.00.

The "common metals" discussed are gold, silver, iron (and steel), copper, lead, and zinc.

The author has brought to bear his own practical experience of forty years in the fields of silver-lead and copper smelting. Experts have coöperated in preparing the chapters on cyaniding gold and silver ores and the metallurgy of zinc.

This edition brings the practice of 1913 up to date. Almost complete rewriting has been necessary.

The usual description of materials and processes has been vitalized in this excellent work by the insertion in the proper places of many data on cost of plant, materials, and operation. While such costs are constantly changing, they are still very useful.

The "Business of Metallurgy" is discussed in a very practical way in Chapters 48 to 50. The suggestions as to organization and management are an appropriate innovation. This side of metallurgy has been neglected heretofore in textbooks.

The list of errata, chiefly in figure reference numbers, is rather long and might cause confusion unless marked in at once.

This is the best metallurgical handbook with which the reviewer is familiar.

Jas. O. Handy

Industrial Hydrogen. By Hugh S. Taylor, D.Sc. (American Chemical Society Monograph Series.) 210 pp. The Chemical Catalog Co., Inc., New York, 1921. Price, $3.50.

This volume is one of the American Chemical Society's series of scientific and technologic monographs. The author states that he has attempted to follow the twofold purposes of the monograph series as decided on by the Board of Editors, and his book not only outlines the fundamental principles and essential chemical facts of the industry of hydrogen production, but also attempts to trace the steps by which the present status of the industry has been reached, to detail what that present status is, and what lines of future development may be anticipated.

The book does not attempt to over-emphasize the engineering side of the subject, but puts more emphasis on the purely chemical side. On the other hand, the author has had in mind the possible application of his work to engineering projects, and has attempted to give the necessary data so that an engineering staff could readily base its calculations for actual plant details. No attempts have been made at giving cost data, or even estimating such, as the author has felt that this was going too far into details of actual commercial operation. It has been his aim, however, to supply sufficient data upon which cost calculations might be made.

The subjects treated in the different chapters are as follows: Hydrogen from Steam and Iron; Hydrogen from Water Gas and Steam; Hydrogen from Water Gas by Liquefaction; Hydrogen by Electrolysis; Hydrogen from Water; Hydrogen from Aqueous Alkalies; Hydrogen from Hydrocarbons; Miscellaneous and By-product Hydrogen Process; The Purification and Testing of Hydrogen. In each case the author has given a general résumé of the subject treated in the chapter without going into a great deal of detail, especially on the plant construction and operation side. He has, whenever possible, discussed fully the chemistry of the processes involved, and such discussion has been in simple and easily understood language. In no case has he gone into the detail that can be found in certain books, such as the British Admiralty "Hydrogen Manual," and the "Hydrogen Manual of the U. S. Air Service," but, on the other hand, the subject has been dealt with in a much more general and comprehensive way, giving not only what has been the practice in the past and is the practice in the present. but also suggestions as to future improvements. It is a book full of most excellent information for the general reader rather than a textbook for an operator of a hydrogen plant.

It is not to be expected that in a book covering so wide a field some errors would not creep in, especially when the author has had necessarily to deal with branches of the subject with which he has had no practical experience. These errors, however, are not serious. The book is an extremely useful one, and should be in every chemical laboratory.

R. B. Moore

American Sulphuric Acid Practice. By Philip deWolf and E. L. Larison, with a special chapter by W. M. LeClear. vii + 270 pp. McGraw-Hill Book Co, Inc., 1921. Price, $3.50.

This proves to be an interesting and suggestive book whether for the beginner or the specialist. Many of the illustrations are from photographs or working drawings and, generally speaking, the book has the advantage of a fresh point of view on the sulfuric acid industry, *i. e.*, the point of view of men who make sulfuric acid in the open surroundings of the metallurgical field and not in the secret star chamber of the chemical field.

The novice should, however, accept many of the statements made with reservations. The historical introduction contains numerous errors. From the technical point of view the book is open to the same criticism. Contrary to our authors' belief, contact process yields are, on the average, probably no better than in good chamber practice and it is difficult to make them as good as are obtained in the best chamber practice. One would be compelled, according to our authors, to believe that oxygen carriers were not actual catalyzers, and that "fume" is not properly fume at all because it is not a true gas, and that high concentration fuming acid plants must be located in the driest climate possible. Something of the same carelessness appears in the authors' use of the English language: "Fuming acid has high melting points, the exact varying with the strength." In spite of the dual authorship, "I" and "we" are used interchangeably. Such blemishes, however, do not seriously interfere with the usefulness of the book.

More critical errors are not lacking: It is stated that "Even with the most careful handling somewhere about 2 to 3 per cent of sulfur will remain in the cinder from roasting pyrites." With good pyrites and careful handling this can be reduced considerably below 1 per cent. Again, it is doubtful if, to test acid bricks for a Glover tower, it is sufficient merely to immerse them in sulfuric acid and then to allow them to weather for a few weeks. Also, direct-connected immersed centrifugal pumps were used in 1905 for handling acid, instead of "put into use during the past three or four years."

On the whole, however, the book is a valuable contribution to the literature of the art.

WM. M. GROSVENOR

Soaps and Proteins—Their Colloid Chemistry in Theory and Practice. By MARTIN H. FISCHER, with the collaboration of GEORGE D. MCLAUGHLIN AND MARION O. HOOKER. ix + 272 pp. John Wiley & Sons, Inc., New York; Chapman & Hall, Ltd., London, 1921. Price, $4.00, net.

The chemical and physical relations existing between fatty acids and their salts and proteins and their salts led the author to investigate the former in order that through analogy he might better understand the proteins and their biological relations.

As indicated in the title, it is the evident intent of the author to treat everything on a colloid basis. The book deals with theoretical and experimental work on the colloid chemistry of soaps, with the author's version of the colloid chemistry of soap manufacture, and with the analogies in the colloid chemistry of soaps, protein derivatives, and tissues.

Any scientist has the unquestioned right to coin a new word at any time to meet a new situation, and colloid chemists have exercised this prerogative to the limit. One might even think they have strained it when they can use without blushing such words as lyophilic, gelation, solvation, syneresis, hydrophilic, dispersoid, lyophobic, and a host of others, and feel called upon to use such words as *solution* and *dissolving* in quotation marks and to refer to their use as "in the accepted parlance." It may be admitted that the molecular behavior that is responsible for many qualities of matter is not completely understood, but the word *solution* conveys a fairly definite idea to the everyday chemist, and to fight shy of the property of matter known as *solubility* will deprive one of means of explaining phenomena not otherwise explainable. The author seems to be profoundly neglectful of the law of mass action, and of Berthelot's Law and Gibbs' Phase Rule.

After discussing experiments and opinions of others on "salting out" soaps, the author concludes that:

> Without recourse to too many or too violent assumptions, the following seems the simplest way out. The entire series of changes observed in the salting out of a soap by an alkali or a salt is readily understood if it is assumed that the added neutral salt or alkali hydroxide unites with the solvent to form a hydrate or solvate and that the consequent viscosity changes (including gelation) are dependent upon the changes in viscosity observed whenever one liquid is emulsified in a second.

Here again the author considers that he is dealing with an *emulsion* rather than a *solution*, and does not grasp a rational explanation that is within his reach. For many years the reviewer has recognized that the "salting out" and the "settling" of soaps are simple examples of the phase rule. This seemed so self-evident that he has never thought of publishing it. To any solution of (sodium) soap in water or liquid solution of water in soap, let us add concentrated caustic soda solution, or salt or strong salt solution. At first a small amount of the added substance is dissolved in the soap and water. Soap is nearly insoluble in strong caustic soda or strong salt solution, and after addition of one or the other or both of these, an amount of salt or caustic alkali is present which can no longer remain dissolved in the soap-water phase as a homogeneous system, and a second phase begins to appear. We have now a phase of soap containing water and a little dissolved salt or alkali, and a phase of dilute solution of salt or caustic soda containing, at first, considerable dissolved soap. At this point there is a change in the viscosity. Further addition of salt or caustic alkali renders the soap still less soluble and precipitates most of the soap which was dissolved in the dilute salt or alkaline phase at the first appearance of the phase, and there are now two phases, the lighter consisting of most of the soap and containing some water and dissolved "lye," and the other consisting of "lye" or salt solution in which there is dissolved a small amount of soap. Soaps with low molecular weights are as a rule more soluble and a larger amount of salt or caustic alkali is needed to salt them out.

"Dehydration" is given as an explanation of many phenomena which to the reviewer would seem to be explained more clearly on the basis of solubility. The expression "complete dehydration" is used rather loosely to denote a condition wherein there is a separation of a concentrated soap, by no means free from dissolved water.

Throughout the book the author, after presenting his arguments, sets down in italics statements which might impress one as proved facts or fundamental general truths. Many of these conclusions are sound and have already been generally accepted, but some of them do not seem to follow from the facts or to be in strict accord with them.

This book will not be of service to the soap manufacturer or soap boiler. The chemist will, however, read it with a great deal of interest. It will be strange if he does not often dissent from many statements, but the man who is able to form his own opinions will be well repaid for reading the book, because of the independent thought it is sure to arouse.

MARTIN HILL ITTNER

Nos Usines Métallurgiques Dévastées. Introduction by LÉON GUILLET. 234 pp. La Revue de Métallurgie, 5, Cité Pigalle, Paris, 1921. Price, 25 fr.

Under this title the editors of *La Revue de Métallurgie* have gathered a number of monographs dealing with the wanton destruction of French metallurgical plants carried out by the German army during the war. Most of this destruction cannot possibly be excused on the grounds of military necessity and appears to have had only the firm purpose of systematically ruining the French metallurgical industry.

The monograph is illustrated with numerous photographs showing the conditions of the plants before the war and after the Armistice and will be a lasting witness of the barbarism with which the war was carried out by the Germans in France. Interesting maps are given showing the extent of the destruction and comparison of what the affected area would represent in proportion in such industrial countries as England and the United States. It would make interesting reading for those who believe in the regulation of methods of warfare by treaties and conventions.

J. ENRIQUE ZANETTI

Chemical Warfare. By AMOS A. FRIES AND CLARENCE J. WEST. x + 445 pp. McGraw-Hill Book Co., Inc., New York, 1921. Price, $3.50.

This is an authoritative compilation and treatise prepared by two American officers exceptionally well qualified for the task. The result of the collaboration of these experts is, as might have been expected, a textbook which gives a full and generally dependable account of the history, development, and significance, of these new and terribly potent weapons, and should certainly find a place upon the shelves of everyone interested in the subject, as well as upon those of all army officers.

A Foreword by Major Gen. William L. Sibert, the distinguished engineer who was the first Director of C. W. S. and who remained its guiding intelligence until long after the signing of the Armistice, concludes with the following generous tribute to the chemical profession: "I feel that this book will show that the genius and patriotism displayed by the chemists and chemical engineers of the country were not surpassed in any other branch of war work and that to fail to utilize in peace times this talent would be a crime."

Many chapters of the book are made up in whole or in part of articles and addresses which have appeared elsewhere and are now gathered together in proper sequence. The official reports submitted to the Director by the various Divisions of the Service have been drawn upon freely, as well as the published contributions of those best qualified to speak on the subject.

In a compilation of this character it is not strange that some repetition and duplication occur and occasional minor discrepancies, but these are not serious and do not affect the value of the book.

Some of us would like to have seen rather more space given to the Chemical Service Section, not only because, as the authors point out, "This holds the distinction of being the first recognition of chemistry as a separate branch of the military service in any country or in any war," but also because it was the nucleus of what subsequently became the headquarters staff, or Administration Division, of C. W. S. To it, and not to the Administration Division, belongs whatever credit may be due for securing authority from the Secretary of War to furlough back to war industries and universities those chemists essential to a maintenance of our output of munitions and of trained men, and finally for obtaining the famous order of May 28, 1918, mobilizing the chemists of the country and placing upon the C. W. S. the responsibility for sending them where they could render to their country the maximum assistance.

In the judgment of the reviewer, the following additions would increase the value of the work, and it is to be hoped that they may be incorporated in subsequent editions: (1) A selected bibliography, for those who do not have available that published in "Special Libraries" (November 1919), and (2) an outline of the organization, personnel, plans, and policy of the Chemical Warfare Service.

MARSTON TAYLOR BOGERT

The Vitamine Manual. By WALTER H. EDDY. 121 pp. Williams & Wilkins Co., Baltimore, 1921. Price, $2.50.

This small volume gives a concise survey of the investigations of vitamines made during the ten years they have been known. The essential facts are very clearly and readily presented, and the book will undoubtedly be greatly appreciated, both by those working in the field and those simply wishing accurate information on the subject.

There is first given an especially interesting account of how vitamines were discovered and this is followed by a short chapter on the attempts which have been made to determine the chemical nature of vitamine. It is to be regretted that the brevity of this chapter is due to the absence of positive information along this line. Of the difficulties encountered in such studies, those resulting from the inadequacy of the physiological methods of vitamine testing are especially noteworthy. The author has, therefore, discussed in detail the available methods which have been developed for this purpose, including the recently proposed yeast test which, however, has, so far, not been shown to be specific for vitamine.

From a practical standpoint the information contained in the chapters on the sources of vitamines, the chemical and physiological properties of the vitamines, and how to utilize the vitamines in diets will be found of most general interest. The author's opinion on the recent crusade for the eating of yeast cakes will undoubtedly be appreciated by many.

The concluding chapter describes briefly the diseases that result from vitamine deficiencies, and finally there is given an excellent bibliography of some 560 references.

ATHERTON SEIDELL

Traité de Métallurgie Générale. By LÉON GUILLET. viii + 528 pp. J.-B. Ballière & Son, 19, Rue Hautefeuille, Paris, 1921. Price, paper covered, 40 fr.; limp binding, 50 fr.

This treatise is the first volume of an encyclopedia of mining and metallurgy to be published under the editorship of Léon Guillet. It forms part of a larger undertaking comprising encyclopedias of industrial electricity, of applied mechanics, of civil engineering and public works, and of industrial chemistry. The publication of 200 volumes is contemplated. The purpose is to discuss the most modern solutions of industrial problems based on scientific knowledge. Thirty-two volumes will be devoted to the study of metallurgy, each one written by a well-known expert.

This first book is divided into twenty-one chapters dealing, respectively, with metallurgical operations and their classifications; roasting and calcining; relation between roasting and calcining and the laws of physical chemistry; apparatus for roasting and calcining; smelting; relations between smelting and the laws of physical chemistry; smelting furnaces, distillation processes; relations between distillation and the laws of physical chemistry; distillation apparatus; electrometallurgy, electric furnaces; wet methods and amalgamation; apparatus for wet methods; electrolysis; wet methods and the laws of physical chemistry; apparatus for electrolysis; treatments of ores; casting of metallurgical products, ingots and their defects; slags; utilization of gases and dusts.

It will be seen that the subject is treated exhaustively and in logical sequence. For those who might be surprised that the fuels and the refractory materials are not included in this volume it should be stated that these subjects are to be dealt with separately in the next two volumes of the series.

Those who are familiar with Professor Guillet's writings know that they are characterized by a masterly grasp, breadth of view, clear and methodical exposition. The same qualities will be found in the present volume. The author, while a scientific man, never loses sight of the fact that metallurgy is essentially an applied science and that its value to the world at large depends upon its possible applications to industrial operations. Sound metallurgical operations, however, should rest upon well-known scientific phenomena, and metallurgical progress should be sought along scientific lines. With this in mind the author takes pains to link every metallurgical operation with the teachings of chemistry and of physical chemistry. Not only the student of metallurgy but the teacher as well and the practicing metallurgist should find in this important book much that is instructive, illuminating, and suggestive.

ALBERT SAUVEUR

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

There has recently been a marked enlargement of development plans for the Argentine oil fields and it is claimed that the next few years will see a greater development than has been accomplished since the first well was drilled. (P. 18)

About three-fourths of Guatemala's imports of **paints and varnishes** consist of the ordinary prepared paints, which come chiefly from the United States. (P. 83)

After a long-continued suspension of imports of **chemicals** into Japan, the demand for foreign chemicals is increasing. About 3500 tons of sulfate of ammonia are said to have been ordered from the United States, while demand is brisk for formalin, rosin, and shellac. (P. 84)

A list of Brazilian **oil seed**, fruit, and nut trees and palms, showing the approximate proportion of the oil yield of each plant, has been prepared by the Director of the Museum of the Commercial Association of Para, and copies may be obtained from the Bureau of Foreign and Domestic Commerce. (P. 373)

Under the name of **"Eulan"** a new product of the German chemical industry has been placed on the European market. The base of the new product is reported to be Martius Yellow which, it is claimed, will render wool moth proof. (P. 450)

The production of the Comodoro Rivadavia **oil fields** for 1920 amounted to 1,540,492 bbls., an increase of 20.44 per cent as compared with the year 1919. (P. 843)

In connection with the use of **fuel oil** in Birmingham, England, a spirit of controversy has arisen concerning the calorific efficiencies of coal and oil. The results of the experiments conducted support the claim that a ton of fuel oil is equal to two tons of coal. (Pp. 843–4)

Rulings for marking **imports for Canada** are cited relative to the following subjects: Acids and chemicals, coal tar, dyestuffs, glue, mica, paints and oils, and tanning materials. (Pp. 854–7)

From statistics on hand the statement is made that Burma is capable of producing sufficient **tin** to make the Indian Empire self-supporting as regards this metal, provided the ores be smelted in India. (P. 893)

An act of the Indian Legislature provides that a customs duty shall be collected on all **lac** and refuse lac produced in India and exported to any port beyond the limits of British India or to Aden. (P. 922)

A French decree of November 4, 1921, increases the general rates of import duty on **chloride of potassium** and **potassium sulfate.** (P. 922)

By a recent decree, **alcohol** imported into Greece to be used for heating and lighting purposes can be denatured only upon approval of the Ministry of Finance. (P. 922)

The **Chilean nitrate** year 1920–21 was similar to the preceding 12 months in that it contained a period of optimism and one of depression, but with the important difference that the year 1919–20 began in inactivity and ended at a time when prosperity appeared to have returned, whereas in the following year the spirit of optimism with which the period began proved to be short lived and soon gave way to demoralization, resulting in the most serious crisis which the industry has ever known. (Pp. 927–9)

Under contemplated changes in Spanish tariff increased duties are proposed on a large number of American exports, including all kinds of **petroleum.** (P. 937)

Negotiations have recently been carried on between the owners of the Outokumpu **copper** mines in eastern Finland and some German copper mine owners for the lease of the Outokumpu mines or the sale of the raw ore from them. Experts say that if the mines are worked to their full capacity the production will amount to at least 6000 tons of copper a year, not counting the other products of which the sulfur alone is sufficient to satisfy the requirements of Finland's paper industry. (P. 947)

The Chuling Mining Works, which is working a **lead** mine in Chenping district, recently made its first shipment of lead. (P. 949)

The increase in the production of the French **bauxite** mines has followed closely the development of the aluminium industry. It is thought that the French production of **aluminium** is likely to increase from 25,000 to 30,000 metric tons as compared to 13,500 metric tons in 1913. The probable French consumption of bauxite might then be 200,000 metric tons per year. (P. 963)

The shipments of **petroleum** from the Tampico oil fields for the month of October 1921 reached a total of 16,052,589 bbls. of 42 gal. each, decreasing 1,154,537 bbls. from the September shipments. The decrease was due primarily to a restricted market for oil in the United States. (P. 969)

Much speculation is current respecting the prospect of discovering oil in the Province of Antofagasta, Chile. (Pp. 970–1)

Telegraphic dispatches indicate large American investments in Bolivian **petroleum.** (P. 971)

The **salt** industry of the Union of South Africa is described as being in a serious condition. (P. 973)

A royal Spanish order has been issued authorizing the unrestricted exportation of **olive oil** until further notice. (P. 983)

The island of Curaçao, West Indies, is gaining in importance because of the increasing development of the **petroleum** industry and of the proximity of the island to the new Venezuelan oil fields. (P. 988)

The Chilean government has sent a mining engineer to Iquique to investigate the report of the discovery of the new **nitrate** zone. (P. 989)

Almost contemporaneously with the issue of the mandate of administration for the islands of Nauru and Ocean, was the rediscovery of the great **sulfur** mountain of Vanua Lava in the Banks group of the New Hebrides. This mountain is one vast mass of sulfur, the quantity being 99 per cent sulfur and the balance ash. (P. 991)

The German Potash Syndicate has issued figures placing Germany's production of **potash salts** during the first six months of 1921 at 4,454,261 metric tons, or 497,373 tons of pure potash. (P. 994)

The outlook of the French chemical industry is decidedly brighter. The production of **alcohol** in France during the first 10 months of this year totaled 944,676 hectoliters, an increase of 210,264 hectoliters over that of the same period last year. (P. 1003)

The paralyzation in **iron** production in the North of Spain continues. (P. 1018)

The world's production of **tungsten** in 1920 was as follows: United Kingdom, 94 long tons; Southern Rhodesia, 15 tons; India, 2346; Federated Malay States, 234; New Zealand, 39; and the United States, 193 tons; a total of 2921 long tons. Each of these figures records a substantial decrease from the corresponding aggregate in 1919, which, in turn, was considerably lower than the production in 1918. (P. 1019)

The Esthonian **oil-shale** exploitations are described, including the nature of the shale, production in 1920, utilization as fuel, distillation, and concessions to native and foreign interests. (Pp. 1028–9)

Statistics are given showing the production of two promising **oil wells** in the Tampico district, and the Panuco fields continue prolific. (P. 1030)

At the recent annual meeting of the Agricultural Society at Beziers, a committee was authorized to organize a competition with a view to discovering a practical and economical **motor fuel** with alcohol as the basis of its composition. (P. 1030)

Information relative to **petroleum concessions** in Honduras may be obtained from the Bureau of Foreign and Domestic Commerce or any of its district or coöperative offices. (P. 1030)

A process has recently been patented in Japan for the production of a fiber resembling **artificial silk** from China grass, or ramie. It is intended to patent the process in other countries. (P. 1030)

Trade lists are available in the Commercial Intelligence Division of the Department of Commerce relative to **petroleum** and **mining** companies operating in Egypt. (P. 1034)

General Australian **tariff** revisions or changes are noted with respect to aluminium, lactose, fertilizers, tanned hides, aromatic distilled waters, nonspirituous, tanning and dyeing extracts. (Pp. 1045–6)

CURRENT PUBLICATIONS

NEW BOOKS

Alchemy: Its Science and Romance. J. E. Mercer. 245 pp. Illustrated. Price, $3.50. The Macmillan Co., New York.

Alcohol: Industrial and Power Alcohol. R. C. Farmer. Pitman's Technical Primers. 110 pp. Price, 85 cents. Sir Isaac Pitman & Sons, Ltd., London.

Alkaloids: Some Microchemical Tests for Alkaloids. Charles H. Stephenson and C. E. Parker. 110 pp. Price, $4.00. J. B. Lippincott Co., Philadelphia.

American Pharmaceutical Association Year Book. Vol. 8. 1919. 748 pp. American Pharmaceutical Association, Chicago.

American Society for Testing Materials: Proceedings. Vol. 21. 1921. 1197 pp. Price, paper, $10.00; cloth, $11.00; half-leather, $12.50. American Society for Testing Materials, Philadelphia.

Applied Calculus. F. F. P. Bisacre. 446 pp. Price, 10s. 6d. Blackie & Sons, Ltd., London.

Asphalts and Allied Substances, Their Occurrence, Modes of Production, Uses in the Arts and Methods of Testing. Herbert Abraham. 2d Edition, revised. 612 pp. 208 illustrations. Price, $6.00. D. Van Nostrand Co., New York.

Bacteriology for Students in General and Household Science. Estelle D. Buchanan and Robert Earle Buchanan. Revised edition. 560 pp. Price, $2.60. The Macmillan Co., New York.

Biological Chemistry: Practical Biological Chemistry. Gabriel Bertrand and Pierre Thomas. 348 pp. Illustrated. Price, $3.75. Harcourt, Brace & Co., Inc., New York.

Biophysics: An Introduction to Biophysics. David Burns. 435 pp. Illustrated. Price, $5.50. The Macmillan Co., New York.

Bleaching and Related Processes. J. Merritt Matthews. 676 pp. Price, $8.00. Chemical Catalog Co., Inc., New York.

Chemistry: Enzyklopädie der Technischen Chemie. Fritz Ullmann. Vol. 9. 1921. Urban & Schwarzenberg, Berlin.

Chemistry: Vocational Chemistry for Students of Agriculture and Home Economics. John L. Willaman J. B. Lippincott Co., Philadelphia.

Coal: The Analysis of Coal and Its By-products. S. R. Illingworth and J. Griffiths. 380 pp. Price, 21s. The Colliery Guardian Co., Ltd., London.

Coal Manual for Salesmen, Buyers and Users. Frank R. Wadleigh. 184 pp. Price, $2.50. National Coal Mining News, Charleston, W. Va.

Colloids: Physics and Chemistry of Colloids and Their Bearing on Industrial Questions. Report of a General Discussion held jointly by the Faraday Society and the Physical Society of London, October 25, 1920. 190 pp. Price, 2s. 6d. H. M. Stationery Office, London.

Colloids: Kolloidchemie und Photographie. Lüppo-Cramer. 2d Ed., revised. 112 pp. Price, 7s. 10d. net. Th. Steinkopff, Dresden, Germany.

Contemporary Science. Edited with an introduction by Benjamin Harrow. 253 pp. Price, 95 cents net. Boni & Liveright, New York.

Electricity: The Emission of Electricity from Hot Bodies. O. W. Richardson. Monographs on Physics. 2d Edition. 320 pp. Price, 16s. Longmans, Green & Co., New York.

Electricity: Rays of Positive Electricity and Their Application to Chemical Analysis. Sir J. J. Thomson. 2d Edition. 237 pp. Price, 16s. Longmans, Green & Co., London.

Engineering Steels. An Exposition of the Properties of Steel for Engineers and Users to Secure Economy in Working and Efficiency of Result. Leslie Aitchison. 427 pp. Illustrated. Price, $6.00. D. Van Nostrand Co., New York.

Food Investigation Board. Special Report No. 5. Report on Heat Insulators. Sir Alfred Ewing and Sir Richard Glazebrook, Chairmen. Price, 3s. H. M. Stationery Office, London.

Food: Vital Factors of Foods; Vitamins and Nutrition. Carleton Ellis and Anna L. MacLeod. 500 pp. Illustrated. Price, $5.00. D. Van Nostrand Co., New York.

Glue: The Manufacture and Use of Plywood and Glue. B. C. Boulton. 90 pp. Price, $2.50. Isaac Pitman & Sons, New York.

Industrial Fatigue and Efficiency. H. M. Vernon. 264 pp. Illustrated. Price, $5.00. E. P. Dutton Co., New York.

Industrial Mathematics Practically Applied. Paul V. Farnsworth. 285 pp. Illustrated. Price, $2.50. D. Van Nostrand Co., New York.

Mechanical Handling of Goods; Modern Methods and Equipment for the Mechanical Handling of Goods in and about Factories, Workshops, Warehouses, Stores, Power Houses, etc.; with Data and Numerical Examples from Practice; for Engineers, Works Managers, Commercial Men, Students, and Others. C. H. Woodfield. 116 pp. Illustrated. Price, 85 cents. Isaac Pitman & Sons, New York.

Metallurgy: Handbook of Metallurgy. Carl Schnabel. Translated by Henry Louis. Vol. II. 2d Edition. 867 pp. Illustrated. Price, $7.50. The Macmillan Co., New York.

Mineralogische Tabellen. P. Groth and K. Mieleitner. 176 pp. R. Oldenbourg, München, Germany.

Mineralogy: Manual of Determinative Mineralogy. J. Volney Lewis. 3d revised and enlarged edition. 298 pp. Illustrated. John Wiley & Sons, Inc., New York.

Oil Shales. H. B. Cronshaw. Imperial Institute Monographs on Mineral Resources with Special Reference to the British Empire. 80 pp. Price, 5s. net. John Murray, London.

Organic Chemistry: Theories of Organic Chemistry. Ferdinand Henrich. Translated and enlarged from the revised German edition of 1918 by Treat B. Johnson and Dorothy A. Hahn. John Wiley & Sons, Inc., New York.

Organische Chemie. R. Pummerer. Vol. III. Wissenschaftliche Forschungsberichte, Naturwissenschaftliche Reihe. 182 pp. Price, 10s. 9d. Th. Steinkopff, Dresden.

Patents and Chemical Research. H. E. Potts. 198 pp. Price, 8s. 6d. The University Press of Liverpool, England.

Petrographic Methods and Calculations. Arthur Holmes. 515 pp. Price, $6.00. D. Van Nostrand Co., New York.

Petroleum: The Economics of Petroleum. Joseph E. Pogue. 375 pp Illustrated. Price, $6.00. John Wiley & Sons, Inc., New York.

Physical Chemistry: Die Physikalische Chemie in der Inneren Medizin. H. Schade. 569 pp. Price, 21s. net. Th. Steinkopff, Dresden, Germany.

Temperature Measurement: The Measurement of Steady and Fluctuating Temperatures. R. Royds. 173 pp. 82 illustrations. Price, $4.00. D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES

Aluminum-Copper Alloys Robert J. Anderson. *Brass World*, Vol. 17 (1921), No. 11, pp. 335–38; No. 12, pp. 364–68.

Cellulose: La Fabbricazione Industriale della Cellulosa al Cloro. Suo Svilluppo Presente ed Avvenire. Umberto Pomilio. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 10, pp. 443–50.

Clay: A Study of Some Bond Clay Mixtures. D. H. Fuller. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 11, pp. 902–15.

Cost Accounting: Some Phases of Chemical Cost Accounting. C. B. E. Rosén. *Chemical Age*, Vol. 29 (1921), No. 12, pp. 501–04.

Dyes: Contribution à l'Étude des Colorants de Cuve: Interpretation d'Expériences Executées avec des Colorants de la Dibenzoyldiaminoanthraquinone. M. Battegay and J. Claudin. *Chimie et Industrie*, Vol. 6 (1921), No. 5, pp. 592–95.

Dyes: On the Fastness of Colors. J. Merritt Matthews. *Color Trade Journal*, Vol. 9 (1921), No. 6, pp. 213–20.

Electrochemistry: Notes et Essais sur la Réduction de la Dépense d'Energie dans les Opérations Électrochimiques. Fernand Boitard. *L' Industrie Chimique*, Vol. 8 (1921), No. 94, pp. 437–41.

Leather: Physiological and Histological Studies on Flayed Skins. Alfred Seymour-Jones. *Chemical and Metallurgical Engineering*, Vol. 25 (1921), No. 23, pp. 1051–54.

Leather: Water-Soluble Matter in Vegetable Tanned Hide Bellies. W. J. Chater and D. Woodroffe. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 11, pp. 359–63.

Leather: The Warble Fly Problem. Alfred Seymour-Jones. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 1, pp. 15–26.

Metallurgy: Some Problems in Nonferrous Metallurgy. J. H. Ransom. *The Metal Industry*, Vol. 19 (1921), No. 12, pp. 469–72.

Photography: The Size-Frequency Distribution of Particles of Silver Halide in Photographic Emulsions and Its Relation to Sensitometric Characteristics. II.—The Methods of Determining Size-Frequency Distribution. E. P. Wightman and S. E. Sheppard. *Journal of Physical Chemistry*, Vol. 25 (1921), No. 7, pp. 561–94.

Porcélaines Electrotechniques. O. Boudouard. *Chimie et Industrie*, Vol. 6 (1921), No. 5, pp. 583–91.

Potash: Greensand as a Source of Fertilizer Potash. R. Norris Shreve. *The American Fertilizer*, Vol. 55 (1921), No. 14, pp. 35–36.

Rosin Varnish: The Manufacture of Rosin Varnishes. P. O. Scribe. *Paint, Oil and Chemical Review*, Vol. 72 (1922), No. 1, pp. 10, 14, 15.

Silk in Its Relation to Dyestuffs. Emile Cagliostro. *Color Trade Journal*, Vol. 10 (1922), No. 1, pp. 1–5.

Sulfuric Acid: The Concentration of Sulfuric Acid. John Wilfrid Parkes and Edwin Gillard Coleman. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 22, pp. 257*t*–65*t*.

Tannin: The Official Method of Tannin Analysis—Some Observations and Suggestions. H. C. Reed and T. Blackadder. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 1, pp. 9–15.

Zinc Dust, Its Uses in the Manufacture and Application of Dyestuffs. J. Merritt Matthews. *Color Trade Journal*, Vol. 10 (1922), No. 1, pp. 14–16.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Destructive Distillation of Mixtures of Oil and Coal. J. D. Davis, P. B. Place and G. S. Scott. *Reports of Investigations* **2301.** 13 pp. Issued December 1921.

Dust Reduction by Wet Stopers. D. Harrington. *Reports of Investigations* **2291.** 5 pp. Issued November 1921.

Eleventh Annual Report by the Director of the Bureau of Mines, Fiscal Year Ended June 30, 1921. 133 pp. Paper, 10 cents. December 1921.

Gas Masks for Gases Met in Fighting Fires. A. C. Fieldner, S. H. Katz and S. P. Kinney. *Technical Paper* **248.** 61 pp. Paper, 25 cents.

Lignite Carbonization—Carbonized Residue Briquets. W. W. Odell. *Reports of Investigations* 2298. 3 pp. Issued December 1921.

Miners' Safety and Health Almanac for 1922. Published in coöperation with the U. S. Public Health Service for the use of miners. Compiled by R. C. Williams. 53 pp. Paper, 5 cents. Published December 1921.

Monthly Statement of Coal-Mine Fatalities in the United States, September 1921. W. W. Adams. 12 pp. Paper, 5 cents.

Monthly Statement of Coal-Mine Fatalities in the United States, October 1921. W. W. Adams. 9 pp. Paper, 5 cents.

Precautions to Be Observed in Entering Abandoned Exploratory Shafts and Pits. B. O. Pickard. *Reports of Investigations* **2295.** 3 pp. Issued November 1921.

Present Status of Coal Carbonization at Low Temperatures. J. D. Davis. *Reports of Investigations* **2292.** 11 pp. Issued November 1921.

Procedure for Testing Explosives for Permissibility for Use in Gaseous and Dusty Coal Mines, with Test Requirements, Tolerance Limits, and Schedule of Fees. *Schedule* **17.** 12 pp. Paper, 5 cents.

Properties of Typical Crude Oils from the Producing Fields of Northern and Central Texas, Northern Louisiana and Arkansas. E. W. Dean, M. B. Cooke and C. R. Bopp. *Reports of Investigations* **2293.** 1 p. Issued November 1921.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. *Reports of Investigations* **305.** 23 pp. Issued December 1921.

Storing Carbide with Explosives. C. E. Munroe. *Reports of Investigations* **2280** (Revised). 3 pp. 1921.

Treatment of Tungsten Ores of Boulder County, Colorado. J. P. Bonardi and J. C. Williams. Prepared in coöperation with Colorado School of Mines. *Bulletin* **187.** *Mineral Technology* **26.** 70 pp. Paper, 25 cents.

Treatment of Carbon Monoxide Poisoning. R. R. Sayers and H. R. O'Brien. *Reports of Investigations* **2304.** 4 pp. Published December 1921.

Bureau of Standards

Annual Report of Director, 1921. *Miscellaneous Publication* **47.** Issued December 1921.

Color Sensitive Photographic Plates and Methods of Sensitizing by Bathing. F. M. Walters, Jr., and Raymond Davis. *Scientific Paper* **422.** Paper, 15 cents.

Cutting Liquids. E. C. Bingham. *Technologic Paper* **204.** Paper, 15 cents. Issued January 1922.

Influence of Phosphorus upon the Microstructure and Hardness of Low Carbon Open Hearth Steels. E. C. Groesbeck. *Technologic Paper* **203.** Paper, 10 cents. Published December 1921.

Recommended Specification for Interior Varnish. *Circular* **117.** Paper, 5 cents.

Recommended Specification for Water-Resisting Spar Varnish. *Circular* **103** (2nd Edition). Paper, 5 cents.

Specific Volume of Liquid Ammonia. C. S. Cragoe and D. R. Harper, 3rd. *Scientific Paper* **420.** Paper, 5 cents. Issued October 1921.

Congressional Committee

Potash. Hearing before the Committee on Finance, United States Senate, 67th Congress, Second Session on H. R. 7456. An act to provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States and for other purposes. Tariff Schedule 15—Free List. Part 53. 211 pp. December 29, 1921. Part 54. 406 pp. December 30, 1921.

Phosphate, Oil, Oil Shale, Gas, and Sodium. Joint Resolution extending the time for the performance of certain acts under the Act of Congress approved February 25, 1920, entitled "An Act to promote the mining of coal, phosphate, oil, oil shale, gas and sodium on the public domain," and for other purposes. H. J. Res. 253. January 9, 1922.

Department of Agriculture

Distillation of Stumpwood and Logging Waste of Western Yellow Pine. M. G. Donk, C. H. Shattuck and W. D. Marshall. *Department Bulletin* **1003.** 69 pp. Paper, 15 cents. Issued December 5, 1921.

Drying Crude Drugs. G. A. Russell. *Farmers' Bulletin* **1231.** 16 pp Issued November 1921.

Getting Our Potash. W. H. Ross. Separate **851** from Yearbook of the Department, 1920. 14 pp. Paper, 5 cents.

Improved Method of Making Sugar-Beet Sirup. C. O. Townsend and Sidney F. Sherwood. *Farmers' Bulletin* **1241.** 16 pp. Issued November 1921.

Influence of Relative Humidity and Moisture Content of Wheat on Milling Yields and Moisture Content of Flour. J. H. Shollenberg. *Department Bulletin* **1013.** 12 pp. Paper, 5 cents. Issued December 22, 1921.

Principles of the Liming of Soils. E. C. Shorey. *Farmers' Bulletin* **924** (Reprint). Paper, 5 cents.

Report of the Chemist. C. L. Alsberg. 48 pp. December 1921. (Covering the work of the Bureau of Chemistry for the fiscal year ended June 30, 1921.)

Volume Variation of Bottled Foods. H. Runkel and J. C. Munch. *Department Bulletin* **1009.** 20 pp. Issued December 16, 1921.

Geological Survey

Gold, Silver, Copper, Lead, and Zinc in South Dakota and Wyoming in 1920. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1920, Part I. 6 pp.

Lignite in the Western Part of the Fort Berthold Indian Reservation South of Missouri River, North Dakota. C. M. Bauer and F. A. Herald. Separate from Contributions to Economic Geology, 1921, Part II. 62 pp. Published December 3, 1921.

Lime in 1920. C. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1920, Part II. 12 pp.

Manganese and Manganiferous Ores in 1920. H. A. C. Jenison. Separate from Mineral Resources of the United States, 1920, Part I. 13 pp. Published December 27, 1921.

Microscopic Determination of the Nonopaque Minerals. E. S. Larsen. *Bulletin* **679.** 294 pp. Paper, 30 cents.

Mineral Resources of the United States, 1918. Part II—Nonmetals. R. W. Stone, Geologist in Charge. 1557 pp. Cloth. 1921.

Natural-Gas Gasoline in 1919. E. G. Sievers. Separate from Mineral Resources of the United States, 1919, Part II. 16 pp. Published December 7, 1921.

Ore Deposits of Cedar Mountain Mineral County, Nevada. Adolph Knopf. *Bulletin* **725-H.** Separate from Contributions to Economic Geology, 1921, Part I. 22 pp. Published November 19, 1921.

Ore Deposits of the Salmon River District, Portland Canal Region, Alaska. L. G. Westgate. *Bulletin* **722-C.** Separate from Mineral Resources of Alaska, 1920-C. 24 pp.

Pyrite at the Haile Mine, Kershaw, South Carolina, with a Note on Pyritization at the Brewer Mine near Jefferson. F. C. Schrader. *Bulletin* **725-F.** Separate from Contributions to Economic Geology, 1921, Part I. 15 pp. Published October 21, 1921.

Round Mountain District, Nevada. H. G. Ferguson. *Bulletin* **725-I.** Separate from Contributions to Economic Geology, 1921, Part I. 24 pp. Published November 21, 1921.

Sand and Gravel in 1920. L. M. Beach. Separate from Mineral Resources of the United States, 1920, Part II. 10 pp.

Secondary Metals in 1920. J. P. Dunlop. Separate from Mineral Resources of the United States, 1920, Part I. 15 pp. Published November 11, 1921.

Silica in 1920. L. M. Beach. Separate from Mineral Resources of the United States, 1920, Part II. 2 pp. Published October 11, 1921.

Silver, Copper, Lead, and Zinc in the Central States in 1920. Mines Report. J. P. Dunlop and F. Begeman. Separate from Mineral Resources of the United States, 1920, Part I. 38 pp. Published November 11, 1921.

Superpower System for the Region between Boston and Washington. W. S. Murray and Others. *Professional Paper* **123.** 261 pp. 1921.

Taylor Creek Tin Deposits, New Mexico. J. M. Hill. *Bulletin* **725-G.** Separate from Contributions to Economic Geology, 1921, Part I. 13 pp. Published November 18, 1921.

Public Health Service

Studies on the Treatment and Disposal of Industrial Wastes. *Bulletin* **118.** Paper, 10 cents. 1921.

Tariff Commission

Tariff Information Surveys. Revised Edition, 1921. C-27. Articles in Paragraphs 162 and 163 of Tariff Act of 1913 and related articles in other paragraphs. Zinc Industry. 82 pp. Paper, 5 cents.

Production Costs in Lithopone Industry. First Six Months of 1921. *Tariff Information Series* **24.** 12 pp. Paper, 5 cents.

MARKET REPORT—JANUARY, 1922

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Jan. 1	Jan. 15
Acid, Boric, cryst., bbls	lb.	.12¾	.12¾
Hydrochloric, com'l, 20°	lb.	.01¼	.01¼
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.06¾	.06¾
Phosphoric, 50% tech	lb.	.12	.10
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	17.00	17.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb.	.03½	.03½
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	.07½	.07½
Ammonia Water, drums, 26°	lb.	.07½	.07½
Arsenic, white	lb.	.07	.07¼
Barium Chloride	ton	50.00	50.00
Nitrate	lb.	*.07	*.06½
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works	100 lbs.	2.25	2.25
Borax, cryst., bbls	lb.	.05¾	.05¾
Bromine, pure	lb.	.20	.20
Calcium Chloride, fused, f. o. b. N. Y.	ton	24.75	24.75
Chalk, precipitated, light	lb.	.03½	.03½
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.55	5.55
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.80	3.80
Lead Acetate, white crystals	lb.	.11	.11
Nitrate	lb.	.15	.15
Red American	100 lbs.	.08	.08
White American	100 lbs.	.07¼	.07¼
Lime Acetate	100 lbs.	1.75	1.75
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, tech	lb.	.06	.06
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*52.00	*52.00
Phosphorus, yellow	lb.	*.28	*.25
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.10¼	.10
Bromide, imported	lb.	*.14	*.13
Carbonate, calc., 80–85%	lb.	.04½	.04½
Chlorate, cryst	lb.	*.06	*.06
Hydroxide, 88–92%	lb.	*.06	*.06
Iodide, bulk	lb.	2.90	2.90
Nitrate	lb.	.08	.08
Permanganate, U. S. P.	lb.	*.15	*.14
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.44½	.43½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	*1.85	*1.75
Caustic, 76%	100 lbs.	*3.70	*3.70
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.30	2.30
Bichromate	lb.	.07¾	.07½
Chlorate	lb.	.07½	.07
Cyanide	lb.	.26	.26
Fluoride, technical	lb.	.10	.10
Hyposulfite, bbls	100 lbs.	3.50	3.50
Nitrate, 95%	100 lbs.	2.32½	2.37½
Silicate, 40°	lb.	.01	.01
Sulfide, 60% fused	lb.	*.04¼	*.04¼
Bisulfite, powdered	lb.	.04½	.04½
Strontium Nitrate	lb.	*.11	*.11
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride, 50% sol'n	lb.	.10¼	.10¼
Oxide	lb.	.38	.38
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.08	.08

ORGANIC CHEMICALS

		Jan. 1	Jan. 15
Acetanilide	lb.	*.29	*.29
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.09	.09
Acetylsalicylic	lb.	.75	.75
Benzoic, U. S. P., ex-toluene	lb.	.60	.55
Carbolic, cryst., U. S. P., drs	lb.	.11	.11
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	*.44	*.43
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.14½	.14½
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.24	.24
Tartaric, crystals, U. S. P.	lb.	*.26	*.25
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12½	.12½
Alcohol, denatured, complete	gal.	.46	.43
Ethyl, 190 proof	gal.	4.85	4.85
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap, refined	lb.	.92	.90
Carbon Bisulfide	lb.	.06½	.06½
Tetrachloride	lb.	.10½	.10½
Chloroform, U. S. P.	lb.	*.38	*.38
Creosote, U. S. P.	lb.	.40	.40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.50	2.50
Imported Potato	lb.	.08½	.08½
Ether, U. S. P., conc., 100 lbs.	lb.	.14	.14
Formaldehyde	lb.	*.10½	*.10
Glycerol, dynamite, drums	lb.	.14	.15
Methanol, pure, bbls	gal.	.75	.75
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	1.93	1.93
Potato, Jap	lb.	.06	.06
Rice	lb.	.18	.18
Sago	lb.	.04	.04

OILS, WAXES, ETC.

		Jan. 1	Jan. 15
Beeswax, pure, white	lb.	.33	.33
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10½	.10½
Ceresin, yellow	lb.	.07½	.07½
Corn Oil, crude, tanks, mills	lb.	.06¾	.06¾
Cottonseed Oil, crude, f. o. b. mill	lb.	.06⅞	.06⅞
Linseed Oil, raw (car lots)	gal.	.69	.72
Menhaden Oil, crude (southern)	gal.	.35	.38
Neat's-foot Oil, 20°	gal.	1.25	1.32
Paraffin, 128–130 m. p., ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.50	5.30
Rosin Oil, first run	gal.	.36	.36
Shellac, T. N.	lb.	.65	.65
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.77	.77
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.91	.89

METALS

		Jan. 1	Jan. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.55	4.45
Bismuth	lb.	1.55	1.65
Copper, electrolytic	lb.	.13⅞	.13⅞
Lake	lb.	.13⅞	.13⅞
Lead, N. Y.	lb.	.04¾	.04¾
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	93.00	93.00
Quicksilver, flask	75 lbs. ea.	52.00	52.00
Silver, foreign	oz.	.66¼	.66¼
Tin	lb.	.33	.32½
Tungsten Wolframite	per unit	2.50	2.50
Zinc, N. Y.	100 lbs.	5.15	5.10

FERTILIZER MATERIALS

		Jan. 1	Jan. 15
Ammonium Sulfate, export	100 lbs.	2.60	2.60
Blood, dried, f. o. b. N. Y.	unit	3.50	3.50
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works	unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.75	.75
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American maker's price).

COAL-TAR CHEMICALS

Crudes

		Jan. 1	Jan. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.29	.29
Cresol, U. S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	.07½	.07½
Phenol, drums	lb.	.11	.11
Toluene, pure	gal.	.30	.30
Xylene, 2 deg. dist. range	gal.	.45	.45

Intermediates

		Jan. 1	Jan. 15
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.25	2.25
H	lb.	.90	.90
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.30	2.30
Naphthionic, crude	lb.	.65	.65
Nevile & Winther's	lb.	1.30	1.30
Phthalic	lb.	.38	.38
Picric	lb.	.30	.30
Sulfanilic	lb.	.27	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.17	17
Aniline Salt	lb	.25	.25
Anthraquinone	lb.	1.50	1.50
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.25	1.25
Benzidine (base)	lb.	.90	.90
Benzidine Sulfate	lb.	.70	.70
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.00	.90
Dimethylaniline	lb.	.40	.40
Dinitrobenzene	lb.	.21	.21
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.60	.60
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.35	1 35
Metol (Rhodol)	lb.	3.00	3.50
Monochlorobenzene	lb.	.10	.10
Monoethylaniline	lb.	1.00	1.00
a-Naphthylamine	lb.	.30	.30
b-Naphthylamine (Sublimed)	lb.	1.50	1.50
b-Naphthol, dist.	lb.	.30	.30
m-Nitroaniline	lb.	.85	.85
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	.11½	.11½
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	—	—
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.70	.70
m-Phenylenediamine	lb.	1.10	1.10
p-Phenylenediamine	lb.	1.60	1.60
Phthalic Anhydride	lb.	.38	.38
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	2.00	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.40	.40
Tolidine (Base)	lb.	1.20	1.20
Toluidine, mixed	lb.	.30	.30
o-Toluidine	lb.	.20	.20
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.10	1.10
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Jan. 1	Jan. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Alkali Blue, domestic	lb.	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Jan. 1	Jan. 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	1.10	1.10
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Jan. 1	Jan. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Jan. 1	Jan. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.75	.75

Chrome Colors

		Jan. 1	Jan. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.65	.65
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Jan. 1	Jan. 15
Auramine, O, domestic	lb.	1.80	1.80
Auramine, OO	lb.	3.00	3.00
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	2.25	2.25
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	1.60	1.60
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc	lb.	8.50	8.50
Victoria Blue, base, domestic	lb.	3.50	3.50
Victoria Green	lb.	1.50	1.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of

INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society

Editor: H. E. Howe
Assistant to the Editor: N. A. Parkinson
Associate Editor: Wilkinson Stark (One Madison Ave., New York City)

Advisory Board: H. E. Barnard, J. W. Beckman, A. D. Little, A. V. H. Mory, Chas. L. Reese, Geo. D. Rosengarten, T. B. Wagner

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Advertising Department:
170 Metropolitan Tower
New York City
Telephone: Gramercy 2145

Volume 14 MARCH 1, 1922 No. 3

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Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, $1.00, Canada, Cuba and Mexico excepted.
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Member of Audit Bureau of Circulations

EDITORIALS

On to Birmingham

Leading men in any activity agree that one of the best investments in their experience and a most potent factor in their success has been attendance at meetings of their fellows. Chemistry is no exception. You owe it to yourself to obtain that advantage which comes only from frequent contact with those in your own field. The benefits are cumulative. He profits most who attends with regularity.

It has been seven years since the Society has enjoyed the hospitality of the South. Birmingham is preparing for us, and the industrial region is attractive. Your especial attention is called to the announcement on page 238 in this issue, and we urge you to plan definitely to be among those present.

The Dye Lobby Investigation

Several months have passed since Senator King demanded an immediate investigation of what he described as a wicked dye lobby. Two months have passed since the probe was ordered, after being widened to include the importers of coal-tar chemicals and dyes. After much difficulty the subcommittee has been completed, comprising Senators Shortridge, *Chairman*, Sterling, and Ashurst. Delays, varied with postponements, followed, until we began to wonder whether the Senator had not found vital weaknesses in his case after his charges were stripped of verbose generalities. We understand he has urged that the Committee be empowered to employ counsel to prepare a case against American dye makers. We suspect the Senator wishes he might be given a place on the Committee and allowed to pass upon the case based upon his own charges.

Meanwhile, both the American Dyes Institute and the Synthetic Organic Chemical Manufacturers Association of the United States have stated their willingness to aid in the investigation and to put their facilities at the disposal of the Committee. It does seem that if things were as bad as stated by the Senator the Committee should be well along with its work. As it is, industrial development is being retarded because the thought of executives is now directed away from business by the impending call to appear at the hearing which began on February 20.

Delay may be a part of the plan to harass our industry continually and give time for foreign penetration while we await decisive action.

Speed the investigation!

Popularity versus Security

Those who really understand something of chemical warfare service were pleased when a committee of technical men, of which the President of this Society was chairman, was formed to bring in a well-considered report on the possibility of controlling chemical warfare by resolutions. An Advisory Committee composed of people who are not chemists and who have given no special thought to the science was also appointed. It has been much to the disappointment of many people that the report of the latter committee, not of the former, has been given publicity. From our present information, it appears that the conference made up its mind in advance and without expert advice that chemical warfare should be made the scapegoat, and that such a report as the Advisory Committee made was the kind it would publish. We have been unable to learn just what the technical report recommended, and we call upon the officials of the conference to give it publication.

In discussing the resolutions pertaining to the abolition of chemical warfare, the Secretary of State declared that the proposed action would be a *popular* thing. We cannot help wondering whether in the minds of the delegates popularity may not at times have taken precedence over security. No one would have felt secure in conferring upon the limitation of navies unless the leading naval powers had been parties to the conference. How can we feel secure in cheerfully passing resolutions on the most humane, efficient, and latest development of warfare without those who first used it, and who are best prepared to develop it further, being parties to the action? And if every nation in the world should sign the treaty, what defense could be made if the treaty were broken unless we had continued research? Quoting Mr. Balfour, "No nation, therefore, can forego the duty of examining how such attacks could be properly dealt with and effectively met."

Chemists in particular and thousands of others want to read the report of the technical committee.

An Invitation

The Woman's Department of The National Civic Federation, of which Mrs. Warren G. Harding is the Honorary Chairman, Miss Maude Wetmore, Chairman, Mrs. Rogers H. Bacon, Secretary, Miss Anne Morgan, Treasurer, and Mrs. Coffin Van Rensselaer, Executive Secretary, passed a resolution at their Thirteenth Annual Meeting which is essentially an invitation to the chemists of the country to appear before the various groups of interested women and tell them something of what chemistry in its various phases means to them and to the country. The resolution follows:

> WHEREAS, The science of chemistry and its applications to industry bear directly upon the welfare of the home, the betterment of agriculture, the efficiency of manufacture, the progress of medicine, the surety of national defense, and
>
> WHEREAS, Advance in chemistry is conditioned by facilities for research both as to personnel and equipment, and
>
> WHEREAS, In a democracy an intelligently informed public understanding of chemistry and the chemical industries is a prerequisite for stimulation of the study of the science of chemistry, advancement in research and stabilization and preservation of the chemical industries,
>
> *Therefore be it resolved,* That the Woman's Department of The National Civic Federation approves and urges the immediate and effective presentation of this subject to the women of America, convinced that through such an educational movement the life of the nation will be bettered and made more secure.

For some time chemists have been complaining of the fact that their work is not understood and appreciated, that too few people know what research in chemistry means to industrial progress and national welfare. Some months ago President Smith urged members to speak upon chemical subjects wherever an audience could be found. Here is an invitation. For your own sake, speak!

Our Viewpoint

Let us suppose there is a community where all buy their supplies by mail. Surely they have a right to do so. But suppose the community encourages one of its members to engage in the general store business? They wish to avoid uncertainties, to have better accommodations, establish a line of credit, obtain specialties upon short notice, and enjoy personal contact in their transactions. It seems to us their action morally binds them to give the support implied in their invitation to the local enterprise so long as it deals fairly with them.

A Victory

On February 14, the Senate, without discussion or dissent, passes the Lambert Patent Bill in the form previously approved by the House. The American Chemical Society deserves a large measure of credit for this action, which will make possible such a reorganization of the Patent Office as all industry must have. The coöperation of the Society, led by its patent committee and its untiring chairman, E. J. Prindle, has been most effective.

Let Congress now take prompt and favorable action on tariff so that industry may get under way, and on reclassification of Federal scientific employees, in the interest of public welfare.

In a time of actual need, a large group of scientists, industrialists, and even government officials insisted that Americans must establish a domestic laboratory apparatus and supply industry, advised that investments necessary for development be made, and assured each other that not only did they desire to make America reasonably independent in essentials, but that they were determined never again to be left without an American source of apparatus. Many of these scientists now seem willing to forget the moral responsibility which they assumed at that time, a responsibility which if fulfilled would guarantee the future of the industry. We highly commend the many consumers of scientific and chemical apparatus and chemicals who have actually made sacrifices in order to do their bit in support of American-made goods. If this support is to continue, certain manufacturers must do their part by careful adherence to specifications. We do regret that so large a number of educational institutions (which buy about 70 per cent of the apparatus used and are alone able to purchase standard items in quantity) are tempted to place abroad the quantity orders which would enable any American manufacturer to reduce his costs. Quality is no longer debated, for America has made good. It is merely a matter of price, in which American costs, always higher than European costs, are still further boosted by the exchange situation.

In commercial graveyards one often finds an epitaph relating how the deceased died because he had a single source of supply which failed, or one single customer whom he lost. The present purchasing policy of some institutions seems certain to leave our laboratories in the hands of a European monopoly, and when Europe ceases to work for nothing and board herself, as she must very soon, we shall have the pleasure of paying through increased prices for all her economic blunders, unless we have a competing industry. Our industry is still very much alive and fighting hard to stay. There is ample American competition. We have seen so many instances in which low prices were used temporarily to crush competition and the losses were later retrieved quickly by advanced prices, that the truth requires no emphasis. To-day importation is at an uncertain price, quality in many cases is below pre-war, and adjustments for breakage and errors are unsatisfactory.

We will admit that there is justification for the importation of some specialties, but we urge that these be purchased through reputable established dealers—the dealers who to-day are importing some things only because their customers demand them, dealers who urge American-made materials but who are being required to import for self-preservation. Is your dealer responsible? Do you investigate your source of supply? Cases have come to our notice where the importer, unfamiliar with the requirements of the trade, has guessed at prices, later found himself unable to deliver at the quotation made, and has then simply quit, leaving the laboratory six to nine months behind its own schedule. Some of these importers live in the catalog of others and content themselves with blanket quotations five per cent below any bid, or send out sheets based upon the convenient catalog of an American dealer. They carry no stock, give no service, and often supply worthless material.

American colleges depend for support upon American industries. If the policy of importation of apparatus were followed to a logical conclusion few domestic industries could grow to philanthropic proportions. We often wonder how a college trustee or university regent can clamor for a protective tariff for his business interests and yet sanction wholesale importation of supplies for the school he helps govern. We urge the abandonment of any purchasing policy which seems so certain to kill our apparatus and chemical industry, founded at such cost, and which is equally certain to weaken our established dealers. There are those ready to spend large sums to improve their product. Competition is sufficiently keen to assure fair dealing, reasonable prices, and real service. Why are so many willing to give up the well-tried principle of the square deal?

Our Personal Loss

We first had the privilege of making the acquaintance of Dr. Charles Baskerville at the Annual Meeting of the Society in Boston in 1909, where his ability to work when there was work to be done and play when the time came for recreation made a strong appeal. From time to time afterward we had occasion to discuss many problems with him, some of which were of personal interest and many related to the activities of the Society. We soon came to know that he could be depended upon to work enthusiastically for what he believed was right, and that he was pretty generally on the right side of things. We came to know of his unusual devotion to the interests of the American Chemical Society, and to know that he devoted many hours of tedious labor to the interests of the Society for which no proper acknowledgment was ever made. Only last autumn he devoted himself to the international phase of the New York Meeting. Previously he discharged the duties of Chairman of our Committees on Occupational Diseases and on Business Management with great credit to himself and great profit to the Society. He never seemed too busy to take up any task which he believed to be for the good of chemists, chemistry, and the American Chemical Society, and it was a comfortable feeling to know that we could go to him, discuss our problems fully, and receive a perfectly frank reply to our questions. Dr. Baskerville was one of those whom one comes to love as a result of much work in common. Without him the going will be made a little more difficult.

Authoritative Information

Many difficulties arise from the use of incorrect information, and serious false impressions are sometimes created. To aid in supplying authoritative information, the A. C. S. News Service was established and has done much toward giving the public a better conception of what chemistry really is. The News Service strives to supply authentic stories of chemical achievements that are newsy and thus to crowd out the sensational accounts usually written by those who know nothing of the real facts.

The daily press, however, is not the only offender, and it is even more important that books be written by those who are authorities upon the subjects treated. There are enough good books to read without taking time for the uncertain ones, but popular subjects are frequently seized upon by those who appreciate a business opportunity but lack the requisite first-hand knowledge. Just now vitamins are everywhere before us, and we would call attention to the review in this issue of Professor Sherman's monograph on the subject. It is an authoritative work, where the writer not only is entirely able to stand upon his own reputation, but has the distinct advantage of having been chosen by our Committee on Scientific Monographs for this contribution to American scientific literature.

It is not difficult to learn whether or not a given writer is a leader in his specialty, and the fact that chemistry is becoming of wider interest makes it more necessary for those who are informed to aid in guiding readers generally in their selection of reference books. It becomes our duty not only to use authoritative sources of information ourselves, but to recommend them to others.

The Earning Power of Research

A few years ago the X-ray tube was an erratic apparatus not in any very general use. The research laboratory of the General Electric Company realized that there was a possibility of utilizing pure electronic emission from a hot filament to produce controllable X-rays in a perfect vacuum. They conducted extensive research upon such devices as then existed, and as a result the tungsten target took the place of platinum in the standard gas tube of that day. Research had also to be applied before the laboratory learned positively that available electrons already existed and that there was a possibility of controlling them, as, for example, focusing them on a target. The research has been continued, until to-day practically all the X-ray tubes of the country are made by the company in accordance with the discoveries of the man whose name the tubes bear. The Coolidge tube is also used abroad almost to the exclusion of other types. These remarkable results have been achieved through very careful, accurate, and often discouraging studies of electric phenomena in high vacua, with very pure materials. The perfection of the tube is the nucleus of an annual business, including accessories and generating apparatus used in X-ray work, of from five to ten million dollars a year. The benefit cannot be measured wholly in monetary return, for everyone is familiar with the humanitarian benefits.

Our oldest industries have been the most reluctant in establishing research laboratories. But the experience of a leader may guide the entire industry. Some years ago the Ward Baking Company established a fellowship at the Mellon Institute. The research soon brought results and the application of a more balanced yeast nutrient to the dough gave better fermentation and better bread. It was discovered that the baker can grow yeast in the dough and control fermentation wastes. This conservation amounts to 2 per cent of the flour, 15 per cent of the sugar, and sufficient yeast to make the total saving 45 cents net per barrel of flour used. It is estimated that this process saves American, Canadian, and British bakers not less than $40,000 per day, without detriment to the quality of the bread.

In 1915 a control laboratory was installed with one chemist. To-day there are a variety of control laboratories with twenty-five technical workers. A chemist has frequently saved two months' salary for his employer with a report on samples from a single carload of butter. The control which has been established as a result of research upon the raw materials makes possible uniformity in the finished product. Time, temperature, and other factors which influence fermentation have been established, and since no two carloads of flour are alike the data are vital in determining how fermentation must be varied to secure uniformity. The study of enzymes, proteins, colloids, yeasts, bacteria, and nutrient value is pointing the way to still better bread, higher nutritive values, economy in production, and the elevation of the entire industry. It is no wonder that during these days of industrial depression this pioneer in research as applied to baking has increased the number of its scientific workers. Results continue to justify the increase.

A Request to Authors

We are indeed anxious to make the Journal still more useful to busy men, and to pack into its pages a maximum of information. We bespeak the coöperation of authors.

Hereafter we plan to print a synopsis of the longer articles, preceding the discussion. We want our summaries really to summarize the articles, to save the time of the busy reader, so that he need not read them in their entirety unless he is truly interested. At the same time he can easily obtain a general idea of the work going on in fields not his own. We feel that these synopses should be prepared by the authors themselves. Please make them a part of the manuscript you send in.

Our office has always tried to have literature references complete. This often imposes an unreasonable burden upon our manuscript editor, of work which in all fairness belongs to the author. Most of our authors are careful about this important detail. Be sure never to overlook it yourself.

Our readers are also interested in knowing the official connections of the authors of articles. Unless there is some strong reason why yours cannot be given, include it on the manuscript.

Another small matter is our desire for double-spaced typewritten manuscripts, not carbon copies. By the time single-spaced or carbon copies reach the printer they may be almost illegible. We also wish more and better illustrations. Read the instructions which we printed at the beginning of "Original Papers" last year.

In order that publication may be given to as large a number of papers as possible, we venture to suggest that authors practice condensation wherever it is possible without weakening the article. It seems to us, for instance, that when most papers on methods of analysis have given enough detail to permit another to duplicate the work, have noted applications, and given conclusions, they have fulfilled their mission. We wish to give important articles ample space, and we also wish to have space available to allow a very broad field to be covered. We feel certain of your coöperation.

Hydrogen Peroxide: Its Manufacture and Preservation[1]

By Paul Poetschke[2]

The L. D. Caulk Co., Milford, Delaware

A detailed account is given of the various stages in the manufacture of hydrogen peroxide from barium peroxide.

The most difficult problem confronting the manufacturer is to secure a product of reasonable stability, so that it will retain its effectiveness until used by the consumer. Experiments in which peroxide was stored in the dark and in varicolored light showed that the solutions keep infinitely better in the dark; orange and red light afford some protection; blue light causes the greatest deterioration.

Manufacturers have not given sufficient attention to the selection of glass bottles of suitable quality for bottling hydrogen peroxide. Carefully conducted experiments confirm the fact that traces of alkali dissolved from the bottle cause rapid deterioration of the peroxide. The interesting fact is that the quality of the glass has a remarkable influence, some bottles causing rapid deterioration while others show but little effect.

Preservatives such as acetanilide retard decomposition but are not uniformly effective. Other factors, such as the character of the glass, exposure to light, acidity, and traces of organic matter often overbalance the restraining effect of the preservatives. Quinine sulfate has many advantages over acetanilide, particularly in that only one-tenth as much is required, and no foreign odor or discoloration results. A mixture of benzoic and salicylic acids is also effective.

Storage in glass bottles of suitable quality and exclusion of light are far more effective in restraining decomposition than are any of the preservatives studied.

HYDROGEN peroxide was discovered in 1818 by P. Thenard, who produced it by the action of dilute acids upon barium peroxide in the presence of water. With certain modifications, adapted to production on a commercial scale, this process is commonly employed at the present time for making medicinal and technical hydrogen peroxide.

The methods of preparation of medicinal and technical hydrogen peroxide are similar, except that phosphoric and sulfuric acids are used for the former, and hydrochloric acid is used in place of phosphoric acid for the technical grades. A further distinction is that materials of greater purity and much greater care and refinement in processes are necessary in preparingthe medicinal product. A knowledge of the process used for making the medicinal article, because it requires greater care and skill, will enable one readily to adapt the process to the manufacture of the technical product.

As actually carried out in practice the manufacture of hydrogen peroxide is perhaps as troublesome as many other industrial processes which appear simple enough when carried out on a laboratory scale. If we had a stable substance to deal with there would be little occasion for presenting this paper, but the fact is that hydrogen peroxide has the peculiar property of decomposing upon the slightest provocation during manufacture and after it is bottled.

Chemicals Required

The chemicals required for the manufacture of medicinal hydrogen peroxide are: barium peroxide containing approximately 90 per cent BaO_2 and as little chloride as possible, phosphoric acid 85 per cent, U. S. P., a good grade of concentrated sulfuric acid, pure barium hydroxide, and distilled water.

Equipment Required

A considerable amount of equipment is required for a hydrogen peroxide plant and the type used depends largely upon the volume produced and the amount of money available for the purpose. The plants that have been in existence for many years often continue to use old-fashioned equipment merely because it is producing and replacement for more up-to-date appliances involves expense. The following general statement of the principal equipment required is all that is necessary:

1—A bin, hopper, and chute for holding and discharging the barium peroxide, all of which may be constructed of wood.

2—Mixers for washing and hydrating barium peroxide, consisting merely of iron tanks provided with heavy mixing blades.

3—A chute leading from the mixers to a small mixing tank.

4—A small mixing tank to keep the hydrated barium peroxide stirred before adding it to the reaction tank.

5—A reaction tank constructed of wood, having a wood mixing paddle or stirrer and lead cooling coils arranged around the sides of the tank. The coils are arranged so that cold water may circulate through as many coils as may be desired.

6—A lead-lined tank for dilute sulfuric acid.

7—A stoneware tank for phosphoric acid.

8—Large filter press for filtering out the barium sulfate by-product.

9—A tank for treatment of the filtered reaction product with barium hydroxide and a small stoneware tank for dissolving barium hydroxide.

10—Small filter press for filtering out precipitated hydrates and phosphates.

11—A lead-lined tank for precipitation of dissolved barium salts with sulfuric acid.

12—Block tin tank for washings from large and small filter press.

13—Receiving and storage tanks.

14—Bottling and packing plant.

In addition to the above equipment, of which there may be one or more units, the plant may have tanks for treating the by-product for recovery of phosphoric acid and a dryer for drying the barium sulfate. As a rule the by-product barium sulfate containing barium phosphate is washed and the wet material packed directly into barrels and sold to dealers in mineral pigments. For this purpose it should be washed free from acid. There are probably some plants where this valuable pigment is still discharged into the sewer. The possibilities of recovering phosphoric acid and producing a fine wet or dry barium sulfate would certainly warrant attention.

Process

WASHING OF BaO_2—The material should be tested for available oxygen. It usually contains 90 per cent of BaO_2 when fresh. The powder is sifted through a 30-mesh sieve and 3000 lbs. are fed into 720 gal. of clear filtered water, which is stirred while the powder is being added and for 10 min. longer. The stirrer is then stopped and the heavy powder allowed to settle for 5 min., the supernatant liquid being siphoned off. The washing is repeated from three to five times, the last washing being made with distilled water. A mark is made on the mixer and water added to this mark each time after siphoning off. Finally the tank is filled up to this mark with distilled water.

HYDRATION OF BaO_2—The barium peroxide is partly hydrated during the washing. In order to complete the hydration to $BaO_2.8H_2O$ and $BaO_2.10H_2O$ the mixer is allowed to run slowly for 18 to 24 hrs., depending upon the temperature. The hydration requires from 307 to 383 gal. of water, the excess of water being sufficient to reduce the mixture to a heavy creamy fluid. It is very important to hydrate the barium peroxide thoroughly so as to reduce all hard lumps. Gritty particles of unhydrated BaO_2 must be avoided because they cause decomposition to take place during the saturation process.

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[1] Presented before the Division of Chemistry of Medicinal Products at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Director, Department of Chemistry.

SATURATION—The washings from a previous batch, amounting to 300 or 400 gal. and containing from one to two volumes of oxygen, are run into the reaction tank, and 160 lbs. of pure phosphoric acid (85 per cent) are added. The stirrer is started and cold water allowed to circulate through the cooling coils (from one to three coils depending upon the temperature of the water). The stirrer is allowed to run continuously during the saturation; otherwise losses will take place. The $BaO_2.xH_2O$ cream is then run into the mixing tank through the chute and the mixing tank kept filled and contents continuously stirred. About three-eighths of the quantity required to neutralize the phosphoric acid is now run in a stream into the diluted phosphoric acid and the reaction allowed to proceed for 10 min. Another charge of like amount is then added with another interval of 10 min. for the reaction to take place. A sample of the mixture is then tested for any gritty particles of barium peroxide; if they are present, a further quantity of $BaO_2.xH_2O$ must not be added until they are reduced, after which the liquid is tested for acidity and if strongly acid small amounts of $BaO_2.xH_2O$ are added at a time until the acidity is mild. At this stage of the process substantially three-fourths of the phosphoric acid will be neutralized.

An interval of 10 min. is now allowed to complete the reaction and 28° Bé. sulfuric acid added, which should be cooled to room temperature. Sufficient sulfuric acid is added to regenerate 85 per cent of the phosphoric acid.

A further quantity of $BaO_2.xH_2O$ is again added, followed by sulfuric acid, and the operation is continued as outlined for the first stage, with all the precautions previously mentioned. The phosphoric acid is used repeatedly to decompose the $BaO_2.xH_2O$, whereas the sulfuric acid is used to regenerate the phosphoric acid.

During the saturation the temperature is maintained at from 90° to 110° F. by running water through the cooling coils. The batch is not allowed to cool below 90° F. because the reaction is too sluggish, or to heat above 110° F. because excessive loss of hydrogen peroxide will then take place.

A quantity of about 75 lbs. of $BaO_2.xH_2O$ is reserved for finishing the reaction, the rest being added in stages as outlined. When all but 75 lbs. of $BaO_2.xH_2O$ have been added the mixture in the reaction tank will be slightly acid and it must be free from any gritty particles because if the latter are present the entire batch may decompose in a few minutes during the finishing of the saturation. The batch should now test about 18 volumes of oxygen. The 75 lbs. of $BaO_2.xH_2O$ are sufficient to convert all of the acid barium phosphates, $BaH_4(PO_4)_2$ and $BaHPO_4$, into the tribarium phosphate, $Ba_3(PO_4)_2$, which is insoluble in water.

About 5 gal. of distilled water are added to the 75 lbs. of $BaO_2.xH_2O$ so as to render it more fluid, and the mixture in the reaction tank is cooled to 95° to 100 ° F. The diluted $BaO_2.xH_2O$ is fed slowly into the mixture through a 30-mesh sieve, made of brass or bronze wire cloth, until the reaction is neutral. This part of the process must be most carefully conducted because if the reaction is allowed to become alkaline even for a few minutes, considerable loss in hydrogen peroxide will result. If the reaction should go over to the alkaline side a small amount of sulfuric acid must be promptly added. The end reaction must be neutral or very faintly acid. If too acid the mixture will be difficult to filter.

FILTRATION—As soon as the reaction has been properly adjusted the mixture is run through the filter press and collected in the tank. The filter press must be in perfect working order in advance of sending the mixture through because there must be no delay at this stage.

If the process has been carefully conducted about 750 gal. of filtrate will be obtained, testing around 18 volumes of oxygen. The reaction tank and press are then washed with 300 gal. of distilled water, this first washing being collected in the same tank (9). This will yield about 1000 gal. and reduce the strength to about 16 volumes of oxygen.

NEUTRALIZATION—Barium hydrate is dissolved in distilled water in a small stoneware tank by injecting steam into it, yielding a saturated hot solution. This solution (while hot) is added to the hydrogen peroxide solution in tank (9) until the reaction is alkaline, so that litmus paper is turned a purple-violet when dipped into the solution. The precipitate of tribarium phosphate, iron hydroxide, and other impurities is filtered off through the small filter press (10) into tank (11), the filtrate being perfectly clear and bright.

ACIDIFICATION—The stirrer is started in tank (11) and 28° Bé. sulfuric acid added in small amounts at a time which will precipitate all of the soluble barium salts as sulfate. From time to time a sample of the fluid is tested by filtering, adding sulfuric acid to the filtrate, and boiling. Addition of sulfuric acid is continued until the barium salts have been completely precipitated and only a slight excess of sulfuric acid remains.

SETTLING—The precipitated barium sulfate is allowed to settle over night and the clear hydrogen peroxide solution siphoned off through a block tin siphon into a receiving tank. After settling in the tank for a day it is drawn off into a clean storage tank and is then ready for preservation, standardization, and bottling if absolutely clear and bright.

WASHINGS—The large and small filter presses are washed with from 300 to 400 gal. of distilled water immediately after being used for filtering the hydrogen peroxide solution, and the washings are run into the tank (12).

PRESERVATION—Acetanilide is the most commonly used preservative for hydrogen peroxide. The U. S. Pharmacopeia limits the amount added to not more than 0.04 g. per 100 cc., corresponding to the customary three-sixteenths of a grain per fluid ounce, which is the amount usually declared on the label as required by the U. S. Pure Food and Drug Law. As a rule from one-eighth to three-sixteenths of a grain is used for each fluid ounce and the desired amount is added to the solution after precipitating the barium salts or to the solution in the storage tank.

Preservatives are not used in all cases and in some instances unusual preservatives, the presence of which need not be declared on the label, such as caffein and quinine, are used. An analysis of one product revealed the presence of a mixture of benzoic acid, salicylic acid, and acetanilide.

STANDARDIZATION—It is necessary to standardize the solution of medicinal hydrogen peroxide so that it will correspond to the requirements of the U. S. Pharmacopeia. As a rule, there is no difficulty in meeting the requirements, the acidity, strength, and nonvolatile matter requiring the most careful attention. All tests are made in accordance with the U. S. Pharmacopeia methods.

If the hydrogen peroxide is sold under the designation "U. S. P." it is necessary to standardize the solution so as to comply with the requirements. Distilled water is added to adjust the strength to somewhat above 3 per cent H_2O_2 by weight or 10 volumes of oxygen, and the liquid is examined in accordance with the U. S. P. tests.

SPECIAL STRENGTH HYDROGEN PEROXIDE—Stronger solutions of hydrogen peroxide are sometimes sold containing 15 volumes or 30 volumes of available oxygen. The former can be obtained directly by the aforementioned process by avoiding dilution. To make the 30-volume product, the process is "doubled up," so to speak, by using 18-volume hydrogen peroxide instead of washings in the reaction tank and diverting the filter press washings, using only the concentrated filtrate as it leaves the filter press.

BOTTLING—The important point in connection with bottling is to use a sound cork of the best quality and to select a good grade of glass bottle. Packing in cartons is advisable. The corks should be wired.

Effect of Light on Deterioration of Hydrogen Peroxide

STORAGE IN DARK—Hydrogen peroxide solutions deteriorate much more rapidly when exposed to the action of light. The extent to which light influences decomposition is clearly indicated by the results shown in Table I.

Table I

Sample	Original Volume	Per cent Loss in Volume in 7 Wks. Dark	White Light
1	15.07	19.9	83.6
2	16.42	5.4	84.1

In these experiments, glass bottles of the same kind were used and the conditions of exposure were identical except as to exclusion of light.

STORAGE IN VARICOLORED LIGHT—The following experiments were conducted to determine the effect of orange, red, white, and blue light. Incidentally, the influence of glass bottles of different composition of glass and the effect of filtration through paper as compared with settling was determined. All of the test bottles were stored in a specially constructed closet, provided with compartments each having windows of orange, red, plain, and blue glass. The results are given in Table II.

Table II

F = Filtered, original volume 16.08
S = Siphoned, original volume 16.28

Time of Exposure, Days		14		36		56		67	
Method of Clarification		F	S	F	S	F	S	F	S
Bottle A: Color of light	Orange	12.94	14.63	6.03	9.09	3.35	6.86	2.06	5.77
	Red	12.51	14.04	5.93	6.92	3.93	4.08	2.75	2.85
	White	12.04	13.99	5.93	7.58	3.99	5.40	2.71	4.22
	Blue	11.09	12.79	5.16	6.48	3.03	4.41	2.10	3.46
Bottle B: Color of light	Orange	14.63	15.26	10.89	14.63	6.08	12.88	3.17	11.38
	Red	14.61	15.30	10.15	13.71	5.36	11.67	2.71	11.41
	White	12.85	14.55	7.48	10.51	3.18	7.36	1.44	5.17
	Blue	12.38	14.71	7.00	10.02	1.84	7.08	1.15	4.97
Bottle C: Color of light	Orange	14.95	15.24	13.65	14.54	12.52	13.87	11.55	13.27
	Red	14.71	15.26	13.02	14.57	11.34	13.79	10.10	13.23
	White	14.97	15.30	14.00	14.50	12.48	13.51	11.65	12.95
	Blue	14.83	15.16	13.81	14.27	12.60	13.40	11.76	12.73

The results in Table II show very conclusively that hydrogen peroxide filtered through paper deteriorates very much more rapidly than hydrogen peroxide which has been clarified by settling. The hydrogen peroxide lost only 0.20 volume upon filtration, showing that the deterioration is due to dissolved organic matter from the paper acting as a catalyst. This proves definitely that hydrogen peroxide should not be clarified by filtration after it is "sulfated," but should be allowed to clarify by settling. Experience has shown that a worn filter cloth used to filter hydrogen peroxide through a filter press will often introduce enough organic matter to result in a seemingly inexplicable tendency of the hydrogen peroxide to decompose.

If the results in varicolored light are examined collectively, it will be noted that orange light affords the best protection and red next. Blue light causes a more rapid deterioration than white light. There are a few results that are apparently contradictory, but the general results plainly show the above relationship.

The composition of the glass bottle evidently has a pronounced effect on deterioration of hydrogen peroxide. A remarkable difference was obtained with the three kinds of glass bottles tested. The A bottle causes the greatest deterioration, B bottle next, and the C bottle has but little influence. In fact, the hydrogen peroxide in C bottle stood up so well that it might be stated definitely that the glass bottle has more effect on the deterioration of hydrogen peroxide than light or conditions of clarification.

Effect of Glass Bottles on Deterioration of Hydrogen Peroxide

It is well known that alkalies, even the traces dissolved from the glass of the bottle, favor deterioration. However, manufacturers have considered this in the light of an unavoidable difficulty and have not given the matter serious consideration from the standpoint of studying the glass so as to secure glass bottles which would insure the greatest permanency. The experiments on the three bottles, the results of which are given in Table II, clearly indicate that a wide difference exists in the quality of the glass actually used in bottling hydrogen peroxide.

In order to verify these results two bottles made of a borosilicate glass, which was known to be more soluble than ordinary glass, were compared with two bottles regularly employed for bottling hydrogen peroxide. All bottles were filled with the same hydrogen peroxide, made by the barium process and free from any preservative, all of the samples being stored in white light under identical conditions. Table III gives the results of these experiments.

Table III

	Bottle	Original Volume	Per cent Loss in Volume, 7 Days
Borosilicate glass...	A	12.85	29.1
	B	12.88	38.4
Regular glass......	A	12.88	8.2
	B	12.88	9.4

An average of the results on the two bottles of the same kind shows that the more soluble borosilicate glass resulted in deterioration approximately four times as rapid as the regular glass used in the trade. Moreover, the evolution of gas bubbles plainly showed that the decomposition was more rapid in the case of the borosilicate glass. The hydrogen peroxide was titrated in the cold, using methyl orange indicator, with the results given in Table IV.

Table IV

	Bottle	Original Cc. 0.1 *N* NaOH	After 7 Days' Storage Cc. 0.1 *N* NaOH
Borosilicate glass...	A	1.75	Neutral
	B	1.75	Neutral
Regular glass......	A	1.75	1.77
	B	1.75	1.77

These results show that there is a marked difference in the solubility of the glass and that the solution of alkali from the glass resulted in the greater deterioration observed to take place with the borosilicate glass.

Influence of Alkali from Glass on Deterioration of Hydrogen Peroxide and the Effect of Acetanilide

In order to study the effect of the alkali from the glass bottle still more thoroughly, four samples of medicinal hydrogen peroxide, representing the product of four manufacturers, were obtained. Samples supposed to be free from acetanilide or other preservatives were selected. The real object of this was to ascertain, if possible, the reason for the difference in keeping qualities of various brands of hydrogen peroxide and particularly whether the kind and quality of acid or impurities contained in the different brands were responsible for the difference in keeping quality or whether the glass bottles had more to do with the deterioration.

Incidentally, the effect of acetanilide as a preservative was determined, particularly as to whether the restraining effect of acetanilide was similar for different brands or whether the quantity and kind of acid or impurities would alter or influence its effect. Table V gives an analysis of the four brands.

TABLE V

SAMPLE		A	B	C	
Hydrogen dioxide:	Absolute	2.828	2.615	2.620	2.622
	Volumes	9.304	8.603	8.619	8.626
Total acidity, cc. of 0.1 *N* alkali required for 25 cc		2.36	2.36	1.28	2.89
Residue on evaporation, g per 100 cc		0.054	0.082	0.064	0.153
Hydrochloric acid, g. per 100 cc		0.011	0.007	0.015	0.034
Sulfuric acid, g. per 100 cc		0.005	0.012	0.014	0.017
Phosphoric acid, g. per 100 cc		0.029	0.034	0.006	0.060
Silica (SiO_2), g. per 100 cc		0.009	0.023	0.023	0.023

The above samples were tested for relative stability both in the original form and after adding three-sixteenths of a grain of acetanilide per fluid ounce, all conditions of storage in white light being identical. Table VI gives the result of these observations.

TABLE VI

SAMPLE		Volumes Oxygen Original	PER CENT LOSS IN VOLUME IN WKS. 1	2	3	7	11
A	Original	9.304	0.15	10.68	11.21	25.08	39.04
	With acetanilide	9.389	0.30	0.87	0.94	2.23	6.79
B	Original	8.603	15.11	25.58	36.80	67.10	82.68
	With acetanilide	9.001	1.98	3.00	5.23	27.34	63.09
C	Original	8.619	6.45	19.79	29.45	63.45	79.24
	With acetanilide	8.938	1.43	3.33	5.12	15.98	47.07
D	Original	8.626	5.28	14.80	18.15	42.49	57.97
	With acetanilide	8.731	0.64	1.84	2.87	8.03	21.47

The acidity of the different samples was carefully determined by titration in the cold, with 0.1 *N* NaOH, titrating first to methyl orange, and then adding phenolphthalein and completing the titration. The samples were titrated after storage for 1 and 13 wks., with the results given in Table VII.

TABLE VII

			ACIDITY CC. 0.1 N NaOH REQUIRED FOR 25 CC.			REDUCTION OR INCREASE IN ACIDITY AFTER 12 WKS.		
SAMPLE		Time of Storage Wks.	Total	Methyl Orange	Phenolphthalein	Total	Methyl Orange	Phenolphthalein
A	Original	1	2.36	1.07	1.29	−0.16	+0.09	−0.25
		13	2.20	1.16	1.04			
	With acetanilide.	1	2.89	1.18	1.71	+0.99	+0.57	+0.42
		13	3.88	1.75	2.13			
B	Original	1	2.36	0.77	1.59	−0.61	−0.12	−0.49
		13	1.75	0.65	1.10			
	With acetanilide.	1	2.80	0.98	1.82	−1.01	−0.49	−0.52
		13	1.79	0.49	1.30			
C	Original	1	1.28	0.53	0.75	−0.41	+0.01	−0.42
		13	0.87	0.54	0.33			
	With acetanilide.	1	1.71	0.86	0.85	−0.62	−0.49	−0.13
		13	1.09	0.37	0.72			
D	Original	1	2.89	1.18	1.71	−0.08	−0.06	−0.02
		13	2.81	1.12	1.69			
	With acetanilide.	1	2.89	1.18	1.71	+0.36	−0.06	+0.42
		13	3.25	1.12	2.13			

The analyses given in Table V show that the samples are all quite pure; at least no explanation for the remarkable difference in stability is possible from the standpoint of purity or acidity.

Acetanilide (see Table V) has a restraining influence on the rate of decomposition which varies with the different samples. Sample A, which is a widely advertised product, is generally understood to have unusual stability and to be free from preservatives. The fact that the sample gave the best results in the original condition and after the addition of acetanilide naturally led to a question as to the possible presence of a preservative. A liter of the sample was extracted with ether in acid solution and then again after addition of sodium hydroxide solution to render it alkaline. The two extracts were evaporated spontaneously and examined for any ether-soluble preservatives. The alkaline ether extract was found to contain quinine equivalent to 60 mg. quinine sulfate per liter. Owing to the presence of hydrochloric, sulfuric, and phosphoric acids in the product it is impossible to state what salt of quinine was originally used. The presence of quinine in the product was verified recently by examining a sealed sample purchased in the open market in July 1921, and an examination made as far back as November 1912 showed quinine to be present.

A study of the results given in Table VII shows that those products which show an increase or the least decrease in acidity upon storage are the more stable, whereas those which show the greatest reduction in acidity deteriorate more rapidly. This relation is shown in Table VIII.

TABLE VIII

SAMPLE		Per cent Loss in Volume 11 Wks.	Per cent Increase or Decrease in Total Acidity 12 Wks.
A	Original	39.04	− 6.8
	With acetanilide	6.79	+34.2
B	Original	82.68	−25.8
	With acetanilide	63.09	−36.0
C	Original	79.24	−32.0
	With acetanilide	47.07	−36.2
D	Original	57.97	− 2.7
	With acetanilide	21.47	+12.4

It must be remembered that Sample A contained quinine, the presence of which was not suspected when the experiment was started. This explains why the original Sample D which contained no preservative showed a greater loss although the decrease in acidity was less. In other respects the results show that samples containing acetanilide, which are the most stable, show an increase in acidity on storage, whereas unpreserved samples show the greatest deterioration with the largest decrease in acidity.

Acetanilide has a tendency to increase the acidity initially and to increase the acidity continually in the more stable products, while in those products which show the greater losses acetanilide appears to lose this property and actually show a decrease in acidity. This explains the variable results obtained in the effectiveness of acetanilide as a preservative and indicates that the alkali derived from the glass acts as a catalyst and has a greater effect in accelerating decomposition than acetanilide has in restraining it.

The remarkable difference in the rate of deterioration observed in the same sample of hydrogen peroxide stored in bottles of different composition, taken in conjunction with the relation of deterioration to decrease in acidity upon storage as determined in these experiments, shows conclusively that the resistance of the glass to attack by the hydrogen peroxide solution is the most prominent cause of deterioration of hydrogen peroxide. Manufacturers have neglected this important phase of the glass problem, evidently upon the assumption that all glass has a similar effect in causing deterioration, little realizing that a remarkable difference in stability may be secured by careful selection of glass of suitable resistance. A proper selection is best made by studying the resistance of the glass to water and weak acids in conjunction with observations on the rate of deterioration of the hydrogen peroxide upon storage. This is a problem well worth the attention of the bottle manufacturer. As a matter of fact, entirely too little attention is given to the suitability of glass bottles as containers for manufactured products and it is the author's experience that defective glass bottles in many instances have been responsible for the deterioration of manufactured products, particularly solutions of various chemicals, pharmaceutical preparations, and beverages.

PRESERVATIVE EFFECT OF CERTAIN ORGANIC SUBSTANCES UPON HYDROGEN PEROXIDE SOLUTIONS

QUININE SULFATE—The U. S. P. salt was added to hydrogen peroxide solutions of two different strengths made by the process already described. In both cases, 3.5 grains of quinine sulfate were added to 1 gal. of the solution. Three different bottles were used in these tests, the bottles containing the original and treated hydrogen peroxide solutions being exposed to white light under identical conditions. Table IX gives the result of these experiments.

TABLE IX

SAMPLE		Bottle	VOLUMES OF OXYGEN Original	VOLUMES OF OXYGEN After 11 Days	Per cent Loss in Volume
A	Original.........	1	16.44	15.60	5.1
		2	16.44	15.16	7.8
	With quinine sulfate	1	16.67	16.59	0.5
		2	16.67	16.68	0.0
		3	16.67	16.54	0.8
B	Original.........	1	25.68	24.44	4.8
		2	25.68	24.21	5.7
		3	25.68	24.28	5.4
	With quinine sulfate...........	1	26.10	26.14	0.0
		2	26.10	26.21	0.0
		3	26.10	26.18	0.0

These results show that quinine sulfate restrains decomposition of hydrogen peroxide solutions of high strength. It was considered interesting to determine whether a solution of pure hydrogen peroxide which had been stored until considerably reduced in H_2O_2 content would show a similar result and also whether a reduced amount of quinine sulfate would be effective. This constitutes a more rigorous test of its effectiveness than when added to a fresh solution because solutions of hydrogen peroxide which have undergone decomposition are more susceptible to decomposition. These results are given in Table X.

TABLE X

SAMPLE	Description Grs. per Gal.	VOLUMES OF OXYGEN Original	VOLUMES OF OXYGEN After 16 Days	Per cent Loss in Volume
1	$+{}^{7}/_{12}$	5.50	3.39	38.3
2	$+1{}^{1}/_{6}$	5.53	4.22	23.7
3	$+1{}^{3}/_{4}$	5.50	4.62	16.0
4	$+2{}^{1}/_{3}$	5.50	4.72	14.1
5	No addition	5.50	2.28	58.5

The results given in Table X show that addition of quinine sulfate restrains the decomposition of hydrogen peroxide solutions which have already lost considerable oxygen and that the restraining effect is dependent upon the amount added. Moreover, it appears that $2{}^{1}/_{3}$ grains per gallon are as much as need be added for preservation.

It was thought interesting to determine whether quinine sulfate added in the various amounts used in all of these experiments would cause a bitter taste in the product. Organoleptic tests made by seven observers, all of whom were asked to determine whether any of the samples had a perceptible bitter taste, gave results which established the fact that quantities up to the limit tested ($3{}^{1}/_{2}$ grains per gallon) did not contribute any bitter taste to the original quinine-free solutions.

VARIOUS PRESERVATIVES—A sample of hydrogen peroxide made by a prominent pharmaceutical manufacturer was found to contain 11.75 grains of benzoic acid, 0.93 grain of salicylic acid, and 1.28 grains of acetanilide in each gallon of the product. Tests were made to determine the effect of this mixture of substances as compared to the same quantity of benzoic and salicylic acids without any acetanilide.

In connection with the organoleptic tests, it was found that some observers reported that plain hydrogen peroxide solutions had a slightly bitter taste. In fact, this is a property of pure hydrogen peroxide. Addition of 1 grain of saccharin per gallon of hydrogen peroxide solution was found to improve the taste. An experiment was, therefore, made to determine the effect of a mixture of $2{}^{1}/_{3}$ grains of quinine sulfate and 1 grain of saccharin on the stability of hydrogen peroxide (Table XI).

A mixture of benzoic acid and salicylic acid in the quantity used exerts a preservative action, which is not appreciably enhanced by the amount of acetanilide added.

Quinine sulfate and saccharin in the quantities used also show a preservative action, although the results with quinine sulfate alone appear to be better.

TABLE XI

SAMPLE	VOLUMES OF OXYGEN Original	VOLUMES OF OXYGEN After 1 Wk.	VOLUMES OF OXYGEN After 4 Wks.	PER CENT LOSS IN VOLUME 1 Wk.	PER CENT LOSS IN VOLUME 4 Wks.
A + 11.88 grs. benzoic acid 0.92 gr. salicylic acid 1.23 grs. acetanilide per gal.	16.16	15.81	13.95	2.1	13.6
B + 11.88 grs. benzoic acid 0.92 gr. salicylic acid 1.23 grs. acetanilide per gal	25.45	24.98	21.96	1.8	13.7
A + 11.98 grs. benzoic acid 0.92 gr. salicylic acid per gal.	16.08	15.66	13.69	2.6	14.8
B + 11.88 grs. benzoic acid 0.92 gr. salicylic acid per gal.	25.45	24.98	....	1.8	...
A + $2{}^{1}/_{3}$ grs. quinine sulfate 1 gr. saccharin per gal.	16.08	15.97	13.82	0.7	14.0
B + $2{}^{1}/_{3}$ grs. quinine sulfate 1 gr. saccharin per gal.	25.42	24.91	21.63	2.0	14.9
A — No addition	16.00	14.63	10.11	8.5	36.8
B — No addition	25.42	23.89	16.63	6.0	34.5

Ordinarily, 24 grains of acetanilide are added to each gallon of hydrogen peroxide as a preservative. It has been the author's experience that $2{}^{1}/_{3}$ grains of quinine sulfate to each gallon are as efficient a preservative and introduces only one-tenth the amount of foreign substance. Moreover, acetanilide causes the development of yellowish or brownish tint and unpleasant odor. The author's experiments have shown that an odor identical with iodoform is developed in solutions of hydrogen peroxide which contain a slight excess of acid. Quinine sulfate does not cause any foreign odor or color to develop. As mentioned before, quinine is used in one of the most widely sold medicinal hydrogen peroxide solutions, and it certainly has advantages over acetanilide, especially in view of the fact that the law does not require its presence to be declared upon the label of the product.

Du Pont Chemical Fellowships

It is interesting to note, in these days of retrenchment, that the du Pont fellowships in chemistry in twenty colleges and universities throughout the United States are to be continued for the academic year 1922–23. These fellowships were established four years ago, at the time when the war made necessary the development of a self-contained chemical industry in this country.

The fellowships are for graduate work. Recipients must be graduates devoting the major part of their time to the study of chemistry, and are selected by the university authorities, not by the Company.

The plan differs from the usual one for industrial fellowships in that the research is not necessarily to be directed along some line in which the Company is interested, but the student is left free, under the direction of his instructors, to follow whatever line of investigation seems to him most promising.

The institutions which receive these fellowships are:

Brown University, Providence, R. I.
California Institute of Technology, Pasadena, Cal.
University of California, Berkeley, Cal
University of Chicago, Chicago, Ill.
Columbia University, New York, N. Y.
Cornell University, Ithaca, N. Y.
Delaware University, Newark, Del.
Harvard University, Cambridge, Mass.
University of Illinois, Urbana, Ill.
Johns Hopkins University, Baltimore, Md.
Lafayette College, Easton, Pa.
Massachusetts Institute of Technology, Cambridge, Mass.
University of Michigan, Ann Arbor, Mich.
University of Minnesota, Minneapolis, Minn.
Ohio State University, Columbus, Ohio
Princeton University, Princeton, N. J.
University of Virginia, University, Va.
University of Washington, Seattle, Wash.
University of Wisconsin, Madison, Wis.
Yale University, New Haven, Conn.

Rates of Absorption and Heat Transfer between Gases and Liquids[1]

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Within the last few years the introduction of solvent recovery and air-conditioning systems in the chemical industry has focused the attention of engineers upon the general problem of interaction between gases and liquids. The commercial scope of this subject includes many processes, such as the separation of ammonia and light oils from by-product coke-oven gas, the recovery of volatile solvents in the rubber industry, air conditioning for the drying of soap, lumber, leather, etc., and ventilation for hospitals and plants handling certain materials such as paper, cloth, and kodak films. The purpose of this article is to present a mathematical treatment for this type of problem and to give results obtained in certain specific cases.

Up to a short time ago, the only method available for the purpose of predicting or altering the capacity of any specified apparatus which transferred matter or energy between gases and liquids was a very indefinite one gained by the experience of the operator. The necessity of working under variable conditions of liquid or gas supply often increased or decreased capacity or efficiency, and accordingly the experienced operator understood in a qualitative manner how to alter the capacity or function of his own particular unit. In 1916, W. K. Lewis[3] developed an expression for the performance of gas scrubbers and other countercurrent absorption devices. The data on the subject available at that time were very meager, and accordingly the theory could not be given a thorough test. Recently, however, considerable data on the transfer of energy and matter have been obtained on various types of commercial and laboratory equipment, and with the aid of these data and a modified treatment of the theory developed by Lewis, transfer coefficients have been obtained for a number of important cases. For any given piece of apparatus the coefficient is a variable quantity directly influenced by the conditions of operation, and is a measure of capacity and efficiency. This article, therefore, is devoted to the following subjects:

1—A presentation of the theory involved in liquid-gas interactions.
2—A summary of Lewis's mathematical treatment with modifications.
3—A verification of the theory.
4—A presentation of equations showing the effect of operating variables on the coefficients for various types of apparatus.

Theory of Rate of Interaction

The theory involved in this problem is based upon the rates of interaction of the two components for the various conditions encountered in practice.

The rate at which energy or matter is transferred from gas to liquid or vice versa is determined by the general law which governs the flow of heat and electricity. In all cases any definite system tends to adjust itself to a condition of equilibrium, and the rate of this adjustment or interaction within the system decreases as equilibrium is approached. In fact, the driving force or potential of the interaction for any given conditions is directly determined by the distance from equilibrium. For problems in heat flow this driving force is the temperature difference, for electricity the voltage drop, and for liquid-gas interactions it may be either a temperature or pressure potential operating on the transfer of heat or matter.

HEAT TRANSFER—The mechanism of heat transfer between gases and liquids can be illustrated (Fig. 1) by the case of a drop of water at a temperature, *t*, suspended in warmer air at a temperature, T. Heat flows from the air into the water because of the difference in temperature between the two. The actual mechanism is a combination of the two processes of convection and diffusion—convection in the main bodies of the gas and the liquid, and diffusion through the comparatively quiet layers in the surface phases. It is well known that the layer of gas against any solid or liquid surface is almost at rest compared to the mass of gas outside, and it is this so-called "film," through which heat must pass by the slow process of diffusion, which offers high resistance to the flow of energy. Similarly a liquid film exists on the surface of the water drop, and the combination of gas and liquid films in series gives a "two-film" resistance. The flow of heat can therefore be expressed by the formula

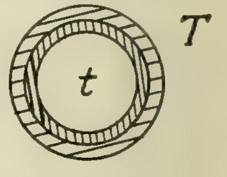

FIG. 1

$$\frac{dQ}{d\theta} = \frac{(T-t)}{R_G + R_L} = \frac{\Delta T}{R_G + R_L}$$

where $dQ/d\theta$ = B. t. u. from gas to liquid per min.
$(T-t)$ = Driving temperature potential in ° F. = ΔT.
R_G = Resistance of gas film.
R_L = Resistance of liquid film.

The values for R_G and R_L will of course vary widely with the specific conditions.

The above method is fundamentally sound in treating the phenomenon as a matter of series resistances. It is customary, however, to handle the calculations from the standpoint of film conductance, *i. e.*, the reciprocal of film resistance. The formula then becomes

$$\frac{dQ}{d\theta} = hA\,\Delta T$$

where hA = Over-all conductance of the two films = $\frac{1}{R_G + R_L}$.
A = Surface area of contact.
h = Over-all conductance per unit area.

Since it is usually impossible to determine A, the area of contact, in any given equipment, the term ha V is substituted for hA, with V the total volume of the equipment where interaction takes place, a the contact surface per unit of volume, and h the conductance per unit of surface. It is obvious that h and a will vary widely with the type of apparatus and the operating conditions, and that they cannot be separated if the actual surface area is not known. In the following general equation,

$$\frac{dQ}{d\theta} = ha\,V\,\Delta T,$$

ha is the coefficient of heat transfer in B. t. u. per cu. ft. per ° F. per min. and is consistently treated as a unit. This equation is the one employed throughout the remainder of the article.

ABSORPTION—The rate of absorption of matter from gas to liquid or vice versa is a process paralleling that of heat

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[1] Received November 17, 1921.

[2] Assistant Professor, School of Chemical Engineering Practice.

[3] "The Principles of Countercurrent Extraction," This Journal, 8 (1916), 827.

transfer. The action can be visualized in the same manner with a two-film resistance to diffusion through the two surface layers, but the driving potential is caused by a difference in pressures or concentrations, rather than by a temperature difference. The previous illustration may be modified for this case by assuming that ammonia is diffusing from a concentrated mixture with air into a dilute solution inside the drop (Fig. 2). Denoting the pressure of ammonia in the gas by P and its concentration in the drop by x, the driving pressure of the diffusion is $(P-\alpha x)$, or $(P-p)$. p is the equilibrium or back pressure of ammonia above a solution of concentration, x, the concentration being determined from the solubility of ammonia in water at the temperature of the drop. In simple cases p and x are related by Henry's Law, *i. e.*, $p = \alpha x$. It is to be understood that this treatment probably cannot be used for problems in which Henry's Law does not hold approximately over the range in question, as, for example, for the absorption of hydrogen chloride gas in water.

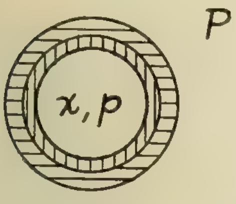

Fig. 2

The general equation for absorption is similar in form to that for heat transfer:

$$\frac{dW}{d\theta} = k'a\,V\,(P-p) = k'a\,V\,\Delta p$$

where $dW/d\theta$ = Lbs. of material absorbed per minute.
$k'a$ = Coefficient of absorption in lbs. of material absorbed per cu. ft. per min. per mm. mercury pressure difference.
V = Volume of apparatus in cubic feet.
Δp = Driving pressure in mm. of mercury.

This equation could also be expressed in the resistance form given under heat transfer.

RELATION BETWEEN HEAT TRANSFER AND GAS ABSORPTION—The similarity between the mechanisms of heat transfer and diffusion of matter between liquids and gases, which has already been pointed out, suggests that the two processes may be directly connected in some simple manner. W. K. Lewis[4] has developed this relationship in a recent article, proving that the ratio of the coefficients $(ha/k'a)$ is practically proportional to the humid heat of the gas. Humid heat is defined as the amount of heat in B. t. u. necessary to raise 1 lb. of inert carrier plus the solute associated with it 1° F. By expressing the Δp pressure difference in pounds of absorbable material per pound of inert carrier instead of in mm. of mercury, the proportionality factor becomes unity:

$$\frac{ha}{ka} = \text{B. t. u. per lb. carrier per } ^\circ\text{F.} = s \text{ (humid heat)}$$

The mathematical derivation of this expression may be found in Lewis's article.

VARIABLES INVOLVED—The main variables affecting heat transfer and diffusion are character of equipment, gas velocity, rate of liquor flow, temperature, and nature of gas, solute, and liquid. Since ha and $k'a$ are connected by direct ratio, it follows that the effect of any variable in design or operation for a definite gas and liquid will be the same for either process.

Character of Equipment—Some of the various types of apparatus used for transferring energy or matter between gases and liquids are packed towers, spray chambers, plate columns, bubbling caps, rotary gas washers, etc. Design is undoubtedly the most important variable to be considered and the coefficients obtained with various machines may be regarded as direct measures of their absorbing or heat transfer effectiveness per unit of volume. It is obvious that any equipment giving large surface area per unit volume will tend to have a high coefficient, other conditions being constant. The influence of character of equipment on other variables will be discussed under the individual variables themselves.

Gas Velocity—The velocity of gas past the liquid surface has an important bearing on the transfer coefficients. High gas velocity exerts a brushing or tearing action on the surface films, reducing their effective thickness and thus decreasing the resistance. The exact nature of this effect can be predicted qualitatively from the character of the apparatus, remembering that the important factor is gas velocity relative to the surface of the liquid rather than the apparent velocity measured past the walls of the equipment. For example, in a coke-filled tower where air is being heated or cooled by water trickling down over the coke, the water is held on the solid coke, and an increase in gas velocity through the tower will cause a corresponding increase in gas velocity past the water. The effect of changing gas velocity should therefore be great for this case. On the other hand, a spray chamber for conditioning air where the gas flows horizontally against a water spray from nozzles illustrates the other extreme. In such a chamber the drops of water are not held on any solid surface, and a definite increase in gas velocity tends to carry the drops along in the air without producing the same increase in the relative motion between gas and liquid. For this case gas velocity should have much less effect than in the coke tower mentioned above. Fig. 3 shows how this effect varies with certain specific designs of apparatus. For ease in comparing effects of gas velocity a power function has been fitted to each of these curves, of the form $ha = kv^n$. The value of this power will be greater in those cases where gas velocity has a greater influence on the coefficient and it will be noted that the results bear out the predictions made above.

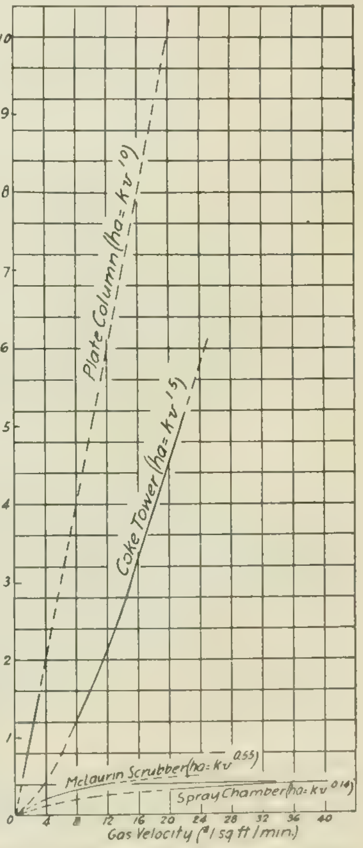

Fig. 3—Effect of Gas Velocity on Heat Transfer Coefficients

Rate of Liquor Flow—The rate of liquor flow through the apparatus should influence the coefficient in two ways. First, an increase in amount of liquor in any given apparatus should increase the surface area of contact up to a certain limit varying with the nature of the apparatus—beyond this limit, a further increase in liquor rate is of little advantage. For example, in a spray device, increasing the liquor rate would produce a greater number of drops of practically the same size, but finally larger drops would result because of interference and coalescence of the smaller ones, and the relative increase in surface of contact would be small. In a packed tower, increase in liquor rate beyond the point necessary to keep the entire packing surface wet would merely cause a thicker layer of liquor with relatively little increase in surface of contact. Second, in the case of packed towers, the increased flow of liquor would in some cases cause more turbulence and motion in the liquor phase, thus reducing the liquid film resistance and increasing heat transfer.

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[4] "The Evaporation of a Liquid into a Gas," to appear in *Mech. Eng.*

Temperature—Temperature has two effects on the total absorption of a definite system. The first of these is obvious, *i. e.*, a change in temperature changes the equilibrium pressure over the solution and hence changes the driving potential. This is completely allowed for in the potential term and does not affect *ka*, the specific coefficient per unit of potential, in the slightest degree. The other effect is a small increase in the coefficient due to increased molecular activity, and should theoretically be proportional to the square root of the absolute temperature of the gas. Liquor temperature is closely correlated with viscosity and is discussed under "Nature of Liquid."

Nature of Gas, Liquid, and Solute—The specific properties of the components in the system have an important bearing on the rate of interaction between the phases. From the physical concept previously presented, certain results can be predicted.

NATURE OF GAS—The relationship between *ha* and *ka* depends almost entirely on the humid heat of the inert gas, and since most gases have the same molecular heat capacity, this relationship should be almost inversely proportional to the molecular weight. Furthermore, the gas film resistance should probably vary in some way with the nature of the gas.

NATURE OF SOLUTE—The rate at which the solute diffuses through a film should vary directly with the velocity of the diffusing molecules. Since this velocity is inversely proportional to the square root of the molecular weight, the coefficient *ka* should vary in the same way.

NATURE OF LIQUID—The important liquor properties to be considered are probably viscosity and surface tension, since these would largely determine the resistance of the liquor film. Experiments on heat transfer from liquids to pipes have shown the coefficients to vary inversely as the viscosity or directly as the fluidity of the liquid, and the same results would be predicted for the conductance of liquid films encountered in liquid-gas interactions. Little has been done on the question of applying surface tension corrections, and it is difficult to predict the exact influence of this variable.

EXPERIMENTAL PROCEDURE

The data from which the experimental coefficients were derived were obtained from two sources, commercial equipment and laboratory apparatus. For both cases the experimental procedure was the same.

Referring to the rate formulas stated above, it is obvious that in all cases three quantities must be determined: (1) the amount of energy or matter being transferred per unit time, (2) the effective volume of the equipment, and (3) the average driving force. From these three quantities the coefficients of heat transfer or diffusion are easily obtained.

In the case of absorption the amount of matter transferred per unit time may be obtained in two ways: by measuring the rate of flow of the gas and analyzing it at both ends of the apparatus, or by measuring the rate of flow of the liquid and analyzing it at both ends of the equipment. For problems in the transfer of heat the requirements are analogous to those stated for the previous case except for the fact that temperatures are used in the place of analyses. One exception is to be noted in this case, namely, the problem of dehumidification for which only the sensible heat change is used in determining the coefficient of heat transfer. The latent heat of condensation is transferred through a process of diffusion and is accounted for in *ka*. Accordingly the change in temperature of the liquid cannot be used as a measure of the heat transfer since this variation is caused by both the heat of condensation and the sensible heat removed from the gas. Therefore, for dehumidification the transfer is always calculated from the gas data.

The total active volume of the equipment is determined by direct measurement. For example, for a packed tower, it is the total volume of the tower minus any inactive portions, such as liquor storage or supports, and for a spray chamber, the total volume is the volume of the chamber minus storage space in the bottom of the chamber. In the case of a bubbling column the total volume is somewhat arbitrary, but for this work the entire available volume between the plates is used to represent this quantity.

The average driving force in any gas absorption equipment is calculated from observed gas and liquor concentrations at both ends of the apparatus. For example, in scrubbing ammonia out of an ammonia-air mixture with water, the average driving force is obtained by calculating the partial pressure difference between the pressure of the ammonia in the gas phase and the equilibrium vapor pressure of ammonia over the liquid at both ends of the apparatus and averaging the differences. In heat transfer the driving force is the average temperature difference between the gas and the liquid throughout the apparatus and is obtained by averaging the corresponding differences at both ends of the apparatus. The logarithmic mean average should be used in place of the arithmetic mean for all cases in which the difference at one end of the equipment is less than half that at the other end. Otherwise the arithmetic mean is used.

EXPERIMENTAL RESULTS

In order to substantiate the theory and to present coefficients obtained in specific cases, the results of numerous tests on different types of apparatus, classified according to type of apparatus studied, are summarized in the following paragraphs. Many of these experiments were designed to show the effect of varying volume and driving potential, and in all cases the formula was found to apply.

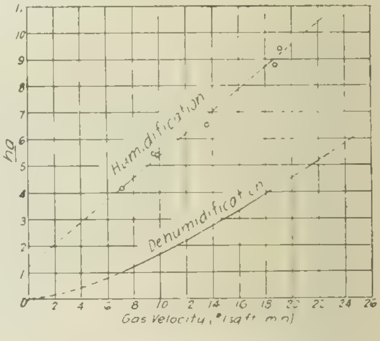

FIG 4—EFFECT OF GAS VELOCITY ON HEAT TRANSFER COEFFICIENTS IN A COKE TOWER
(Data at 20 lbs. water/sq. ft./min.)

PACKED TOWERS—One of the authors[5] ran tests on an experimental tower (1 ft. in diam. × 5 ft. high), packed with 3-in. gas coke, working with air and water and studying humidification and dehumidification. The results may be briefly summed up as follows. In *humidification* (Fig. 4) the heat transfer varies as a straight line function of the gas velocity and is expressed by the equation

$$ha_H = \frac{1}{R_G} = 1.20 + 0.42\,G,$$

in which G varied from 7.1 to 18.7 lbs. of dry air per sq. ft. per min., and *ha* increased from 4.2 to 9.1 B. t. u. per min. per cu. ft. per ° F. temperature difference. The dotted portion of the plot indicates the extrapolated zone. It is inadvisable to extrapolate this equation beyond the limits of the experimental work because the results might also have been expressed by power curves passing through the origin, but values showing this function at low gas velocities could not be obtained because the apparatus as constructed could not be operated over that range. Humidification runs made with variable liquid rate showed that the heat transfer was independent of the water rate. This is explained by the fact that in adiabatic humidification the water remains at a constant temperature, and accordingly there is no heat transfer through the liquid film, thus eliminating one of the resistances. The increase in active surface with increased liquid rate is negligible in a packed tower.

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[5] J. L. Keats, "A Study of Heat Transfer and Diffusion in a Coke Tower," M. I. T. Thesis, June 1921.

In *dehumidification* (Fig. 4) the equation

$$ha_D = \frac{1}{R_G + R_L} = \frac{1}{\dfrac{1}{1.20 + 0.42\ G} + \dfrac{1}{(0.000387)\ (G)^{1.8}\ (L)^{1.54}}}$$

was obtained within the experimental limits of 7.1 to 22.1 lbs. of dry air per sq. ft. per min. and 9 to 43 lbs. of water per sq. ft. per min. Values of ha_D increased from 1.2 to 5.3 and were calculated from the sensible heat lost by the air. The latent heat transfer accompanying the condensation and diffusion of water vapor into the liquid should not be considered here, as this part of the process is actually a diffusion of material rather than of heat. This equation checks up the predicted results fairly well and shows that both gas velocity and water rate have an effect upon the liquid film resistance. The limits of temperatures used did not allow for an appreciable variation in viscosity, and therefore this variable does not appear in the results.

These results show clearly that the coefficient for humidification is always greater than that for dehumidification at the same water and gas velocities. This is explained by the additional liquid film resistance encountered in the latter case.

The twenty-five runs made on this tower checked up the relationship $ha/ka = s$ within an average deviation of 15 per cent. The results were obtained with air velocities much higher than those used in commercial operation, and therefore the power required to force air through the tower was excessive.

MCLAURIN GAS SCRUBBER—Experiments[6] were carried out on an installation of this standard apparatus in order to study humidification, dehumidification, and acetone absorption. For *humidification* the effect of gas velocity is expressed by the equation

$$ha_H = 0.0722\ G,$$

in which G varies from 3.5 to 15.3 lbs. of dry air per min. per sq. ft. maximum cross section and ha_H varies from 0.25 to 1.10. The water rate was held constant at 100 lbs. per sq. ft. per min. This agrees in theory with the results obtained on the coke tower, but the heat transfer values are lower for the McLaurin apparatus because the active area of contact per unit volume is smaller in the latter. The effect of water rate in this case is found to be

$$ha_H = \frac{0.61\ L}{L + 14.0}$$

at 7.58 lbs. of dry air per sq. ft. per min. L varied from 3.4 to 117 lbs. of water per sq. ft. per min. and ha_H varied from 0.12 to 0.54. This equation shows that increased water rate increases the heat transfer coefficient as a hyperbolic function, *i. e.*, rapidly at low liquor rates and less rapidly at higher. This is to be expected in this type of equipment, owing to the change in active surface under varying water rate.

In *dehumidification* the effect of gas velocity on the heat transfer was found to be a hyperbolic function

$$ha_D = \frac{G}{G + 9.07}$$

at 98 lbs. of water per sq. ft. per min. The limits of G were 2.8 to 13.0 lbs. of dry air per sq. ft. per min. and ha_D from 0.18 to 0.60. This equation shows that the addition of the liquid film resistance has cut down the over-all heat transfer. The effect of water rate in this case is also a hyperbolic function

$$ha_D = \frac{0.53\ L}{L + 12.1}$$

with L varying between 13.8 and 110 lbs. of water per sq. ft. per min. and ha_D varying from 0.30 to 0.48. The form of this equation is similar to those obtained above and indicates that water rate probably affects the active surface exposed. The results obtained on this gas scrubber seem to indicate that the heat transfer varies inversely as the viscosity of the water, but positive proof of this fact was not obtained.

All of the runs on humidification and dehumidification checked up the relationship $ha/ka = s$ as well as the results obtained on the coke tower. In the nine runs on acetone absorption the concentration of acetone in the entering air was varied from 0.03 to 0.20 per cent by volume, and the apparatus was run with 8.43 lbs. of air per sq. ft. per min. and 98 lbs. of water per sq. ft. per min. The average value of $k'a$ was 0.0037 lb. of acetone per cu. ft. per min. per mm. mercury pressure difference. In order to compare this value with ha for water vapor, the former had first to be converted to the basis of ka:

$$ka = 0.0037 \times \frac{29}{58} \times 760 = 1.40 \text{ lbs. acetone absorbed per min. per cu. ft. per lbs. of acetone per lb. of carrier,}$$

and then multiplied by the square root of the ratio of the molecular weights of acetone and water to account for the difference in diffusional velocities of the two solutes. In this way $1.40\sqrt{\frac{58}{18}} = 2.52$ (the calculated value of ka for water) which checks up $ha/ka = s$ within 1 per cent, using the ha_H obtained in humidification under the same conditions, and within 20 per cent using the heat transfer coefficient for dehumidification.

PLATE COLUMN FOR ABSORPTION OF AMMONIA—Reynolds and Sanders[7] continued an investigation started by one of the authors on the absorption of ammonia by one plate of a copper rectifying column. This plate had an area of 2 sq. ft. and the chamber was 10 in. high, giving an effective volume of 1.67 cu. ft. Five bubbling caps, each 3.5 in. in diameter and 2 in. high and provided with 40 vertical slots $^5/_8$ in. long were placed on the plate, and runs were made to determine the effect of air velocity, flow of water, water level, concentration of inlet gas, and the addition of a second plate in series.

The results showed that $k'a$ was directly proportional to air velocity, and that it increased only slightly with increasing water rate. Water level (varying between 1.5 and 4 in.), concentration of inlet gas, and addition of a second plate had no effect at all on the specific absorption coefficient. The final equation

$$k'a = 0.00114\ G\ (1 + 0.017\ L)$$

covers a range of velocity from 1 to 3 lbs. of air and from 3 to 19 lbs. of water per min. per sq. ft. of plate, with $k'a$ values ranging from a minimum of 0.0011 to a maximum of 0.0045 lb. of ammonia absorbed per min. per cu. ft. per mm. mercury driving potential.

The important conclusions from this work are (1) that for this equipment operating with ammonia and water at nearly constant temperature, gas velocity is the only variable exerting a marked effect, as predicted by theory,

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[6] M. B. Littlefield, P. C. Merrill and C. C. Stewart, M. I. T. Thesis, May 1921.

[7] "The Absorption of Gases by Liquids," M. I. T. Thesis, May 1920.

(2) that liquor rate increases the coefficient only by creating greater turbulence and causing more uniform mixing, and (3) that since the coefficient is constant at varying liquor levels on the plate, a large part of the absorption must take place in the spray above the main body of the liquor. Indeed, it seems probable that increased gas velocity helps absorption chiefly by causing a greater spray formation.

ABSORPTION OF AMMONIA IN A LABORATORY BUBBLING DEVICE—Harrop and Carlson[8] constructed a glass apparatus for absorbing ammonia in which a dilute ammonia gas mixture bubbled up through a 4-in. Büchner funnel into water which was fed and discharged from the apparatus at a constant rate. They studied the effect of air velocity and of concentration of ammonia, obtaining the same sort of results as found in the work on the plate column, *i. e.*, the coefficient varied directly with gas velocity and was unaffected by changes in concentration. The effective volume of their bubbler was about 0.045 cu. ft., and with gas velocities from 0.4 to 0.9 lb. of air per sq. ft. per min. the values of $k'a$ increased from 0.0012 to 0.0028 following the equation

$$k'a = 0.0037\ G.$$

These results serve to check the effect of gas velocity in bubbling equipment. It will be noted that the above equation gives values of $k'a$ higher than those obtained in the equation for the rectifying column at the same gas velocity. This is due to the fact that the bubbler construction gave more surface area for interaction and hence had more absorption capacity per unit of volume.

CENTRIFUGAL SPRAY CHAMBER—The writers were permitted the use of some unpublished data on the operation of a centrifugal spray chamber, and have calculated the heat transfer and absorption coefficients obtained in the two series of tests. The runs were made with varying gas and liquid velocities. In the first set the chamber was used to cool hot condenser water with air and in the second set to absorb ammonia from air with water.

The exact equations cannot be stated because of the confidential nature of these data, but the effect of gas velocity was considerably less than in the case of packed towers or of bubblers and of the general nature exhibited in the air-conditioning chamber discussed later. The general design of the apparatus makes this result reasonable, since the liquid is in the form of an unsupported spray of droplets. Increased water rate raised the coefficient rapidly at the start, but no further increase could be observed after a certain limit. Above this limit a greater rate merely formed larger drops without appreciably increasing the surface of contact.

The most important conclusion from these data is obtained by comparing heat transfer in the first set with absorption of ammonia in the second with other conditions constant. The calculated value of ha/ka differs from the humid heat of the gas by about 30 per cent, which further checks the validity of the relationship between heat transfer and absorption.

AIR-CONDITIONING CHAMBERS—Tests were run on humidifying and dehumidifying air in three-stage and four-stage horizontal conditioning chambers with varying air velocities. Each stage was 9 sq. ft. in area and 7 ft. long, and was equipped with nozzles spraying a constant amount of water at constant pressure against the air stream (details of construction confidential). The first stage of the series acted as a humidifier and the others as dehumidifiers, with water recirculating through the sprays and feeding from one chamber to the next countercurrent to the flow of the air.

The results of this work show the effect of gas velocity on heat transfer and a comparison of humidification and dehumidification under similar conditions. As stated under the discussion of packed towers, the resistance to heat flow in adiabatic humidification is due solely to the gas film, since the water remains at a constant temperature. For this case

$$ha_H = \frac{1}{R_G} = 0.64 + 0.037\ G.$$

In dehumidification

$$ha_D = \frac{1}{R_R + R_L} = \frac{1}{\dfrac{1}{0.64 + 0.037\ G} + \dfrac{1}{0.35 + 0.0040\ G}}.$$

The values of ha_H are from 1.4 to 2.3 and of ha_D from 0.33 to 0.43 with air velocities increasing from 20 to 45 lbs. of air per sq. ft. per min. A plot of ha against gas velocity showing one line for humidification and another for dehumidification would be similar in general nature to the one already presented for the results on the coke tower. Reference to Fig. 3 shows that air velocity has only a slight effect on heat transfer in this equipment.

SIGNIFICANCE OF RESULTS

In summarizing the results of this investigation the following facts are to be noted. The treatment suggested for liquid-gas interactions has been checked up by experimental data obtained from various types of laboratory and commercial equipment and has been found to apply in all the cases studied. The general formulas

$$\frac{dQ}{d\Theta} = ha\ V\ \Delta T$$

$$\frac{dW}{d\Theta} = ka\ V\ \Delta p$$

show that the rate of transfer varies directly with the active volume and the driving potential. The effect of other variables is accounted for by changes in the transfer coefficients ha and ka. These coefficients are mainly influenced by the type of equipment. In addition, for any specified unit the coefficients will vary with operating conditions such as gas velocity, liquor rate, temperature, etc. Of these operating variables gas velocity has shown the most marked effect in all cases which have been studied.

The following table gives the value of transfer coefficients obtained on some of the important types of equipment under the stated conditions.

COEFFICIENTS FOR VARIOUS TYPES OF EQUIPMENT

APPARATUS	ha (Dehumid.)	$k'a$	Gas Vel. (Lbs./Sq. Ft. /Min.)	Water Rate (Lbs./Sq. Ft. /Min.)
Coke tower	2.20	0.0072	12	20
McLaurin gas scrubber	0.57	0.0019	12	100
Spray chamber	0.29	(0.00095)	12	20
Plate column	(5.50)	0.0183[1]	12	20
Laboratory bubbler	(13.7)	0.045[1]	12	0.5

[1] Extrapolated value. Coefficients given in parentheses were obtained by using $ha/ka = s$.

In applying this method for designing absorption or heat transfer equipment it is obvious that the specific transfer coefficients, ha and ka, are not the only criteria to be considered. From an economic standpoint factors such as investment, labor, repairs, and power have a vital bearing. For example, it is impracticable to operate coke towers at very high gas velocity merely to obtain good absorption, since the increased friction drop through the system makes power costs prohibitive. It is therefore hoped that a continuation of the present work will modify the method of treatment and eventually allow transfer coefficients to be expressed per unit of cost.

The value of the method in its present form is twofold. First, it shows how a change in the operating variables will affect the capacity and efficiency of a definite industrial unit. In the second place, it helps the engineer to design new equipment and to predict the performance of a given type of apparatus on any heat transfer or absorption problem from data obtained in operating tests on the same type of machine. The theory is based on the fundamental principles of heat transfer and absorption, and serves to correlate and classify the performance of apparatus designed for these purposes.

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[8] "A Study of the Rate of Gas Absorption," M. I. T. Thesis, May 1920

The Colloid Content of Vegetable Tanning Extracts[1,2]

With Attempts to Correlate Astringency with the Potential Difference of the Particles against the Aqueous Phase

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As recorded in the following paper, measurement of the potential differences of certain vegetable tanning extracts shows that the order of these values is approximately the same as the order of their degrees of astringency. The potential difference increases with dilution of the extract, decreases with rising acidity, and is increased by dialysis of the extract. These simple manipulations suggest possibilities for a more intelligent use of these extracts in vegetable tanning.

Precipitation tests were made on the extracts with various electrolytes. The conduct of the extracts shows that there is a large amount of colloidal matter present, that it belongs to a type of dispersion with properties between the intermediate and hydrophilic dispersions, and, hence, that the measurements reported in the first part of the paper are justified.

From the colloidal point of view, vegetable tanning extracts constitute an unexplored field, and the authors believe that the precipitation graphs included in this article will prove of value when interpreted in the light of future research.

ASTRINGENT properties of vegetable tanning extracts vary enormously, generally depending upon the source of the extract. If the fundamental reason for this variation could be discovered, rapid progress would be effected in the use of various extracts in vegetable tanning. It would be possible by varying the astringency of a given extract by simple chemical treatment to render an extract suitable for any process, thus avoiding the employment of a given extract or mixture of extracts for making a given kind of leather.

The simple theory of vegetable tanning proposed by Procter and Wilson[4] is based on a mutual neutralization of the opposite electrical charges of the colloidal tannin particles and the hide colloids. If this theory is correct the electrical charge of the tannin particles should be greater for an astringent extract than for a mild one.

The authors have endeavored to determine the potential difference of the tannin particles in various vegetable extracts against the aqueous phase, *i. e.*, the difference in potential of the negative electrical charges on the particles against the positive charges of the ions in the water immediately in contact with the particles.

APPARATUS

The method used for the determination was the U-tube electrophoresis technic as described by Burton.[5]

The U-tube had limbs about 20 cm. in length and 2 cm. in diameter. The lower half of each limb was graduated in fifths of centimeters, from 0 at the top to 10 cm. at the lower portion. In the bottom of the bend of the U-tube was sealed a delivery tube with stopcock, bent upward and ending above the upper levels of the limbs in a funnel, for the purpose of filling the tube with the solution. The platinum electrodes were sections of cylinders, not spirals as used by Burton.

Before operating, the effective distance through the bend of the tube was measured, so that the potential gradient per centimeter could be calculated. The conductivities of known columns of 0.02 M KCl solution through the graduated portions of the tube were determined, and the conductivity between the lowest graduated marks on each limb through the bend was compared with these values. The effective distance through the bend was found to be 9.9 cm.

The conductivities of the solutions of all extracts were determined in the usual type of Wheatstone bridge apparatus with a Freas conductivity cell.[6] Solutions of potassium chloride of the same conductivity were superimposed upon the columns of the extract in the U-tube. The concentrations of chloride required for given conductivities were based upon the figures of Noyes and Falk,[7] and were obtained by plotting their specific conductance values against concentration of potassium chloride. When the conductance of a tanning solution was obtained the corresponding concentration of potassium chloride was found by merely reading from the curve of Noyes and Falk's data.

All measurements of conductivity and electrophoresis were made at 25° ±0.005° C. by submerging the cells and tubes in a large Freas water thermostat which contained 80 gal. of water at the temperature stated.

METHOD

The potassium chloride solution of the same conductivity as the extract to be studied was poured through the funnel and allowed to flow into the bend of the U-tube. The stopcock was closed, the excess chloride remaining in the delivery tube was removed, and the delivery tube was filled with the tanning extract. By gradually opening the stopcock, the extract was allowed to flow very slowly into the bend so that it would not mix with the layer of potassium chloride solution. The final result was a U-tube filled through the bend and up the limbs with extract, with a 2-cm. layer of potassium chloride solution on top of each column. By careful manipulation, the interfaces between colloidal dispersion and electrolyte solution were fairly sharp.

The platinum electrodes were carefully inserted, both to the same level, and submerged in the potassium chloride

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[1] Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 383 from the Chemical Laboratories of Columbia University.

[3] Assistant Professor.

[4] *J. Chem. Soc.*, **109** (1916), 1327.

[5] "Physical Properties of Colloidal Solutions," Chapter VII (1916).

[6] Emer and Amend, 1920 Catalog, No. 5202.

[7] *J. Am. Chem. Soc.*, **34** (1912), 454.

solution, not coming in contact with the tanning solution. The tube was then immersed in the water bath, and the electrodes were connected with a 115-volt direct house current.

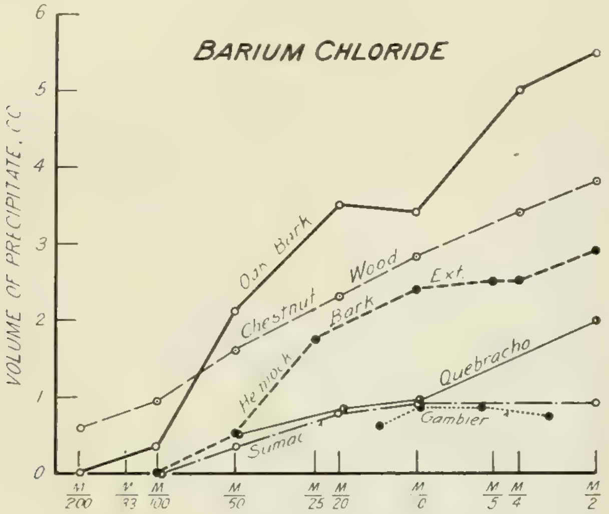

FIG. 1

The current was passed for 5 min., reversed, and passed an additional 5 min., in order to flatten the interfacial surfaces. The current was then passed through for 20 min., and the displacement noted during this period. From the values obtained the velocity of migration could be calculated.

The potential differences of the double layers of the particles were calculated by means of the well-known formula of Lamb,[8] as applied by Burton:[9]

$$P.\ D.\ = \frac{4\pi\eta v(300)^2}{KX}$$

where P. D. = Potential difference in volts.
η = Viscosity of dispersion medium (in this case water at 25° = 10.2×10^{-3}).
v = Velocity of migration in cm. per sec.
K = Dielectric constant of dispersion medium (K of water = 80).
X = Potential drop in volts per cm.

MATERIALS

The vegetable tanning agents listed in Table I were kindly analyzed and supplied by Mr. John Arthur Wilson.

For the electrophoresis measurements, the concentrations of tanning solutions were such that they contained 1 per cent tannin according to the above analyses, and the solutions were centrifuged for 5 min. to remove coarse suspended matter. The tannin percentages were determined by the A. L. C. A. official method. They are merely arbitrary values which are used for purposes of commercial evaluation of vegetable extracts and, as shown by Wilson and Kern,[10] do not represent the true values. When this work was commenced, however, they were the best figures available. Actually, with the exception of quebracho and osage orange, the solutions all contained about 4 g. total solids per 100 cc.

RESULTS

All the experimental data, accumulated over a 2-yr. period, cannot be recorded here. The following results are typical:

TABLE I—MATERIALS USED

	100 Per cent				
		Insol.	Soluble		
	Water	Matter	Nontannin	Tannin	Ash
Solid quebracho extract....	22.82	7.73	6.30	63.15	0.58
Hemlock bark extract.....	52.58	6.21	18.36	22.85	1.19
Hemlock bark (Wis.).....	...	...	...	...	...
Gambier extract..........	48.49	10.22	17.51	23.78	3.51
Cube gambier............	9.30	34.70	26.00	30.00	23.40
Palermo sumac...........	9.39	45.39	18.33	26.89	9.40
Sumac extract...........	51.32	2.19	22.77	23.72	4.11
Chestnut oak bark extract	52.00	2.46	19.89	25.65	1.51
Larch bark extract.......	51.41	5.45	21.04	22.10	1.13
Oak bark extract 1.......	52.78	2.59	17.05	27.58	1.56
Oak bark extract 2.......	54.39	1.76	18.10	25.75	1.38
Aurantine (osage orange).	7.30	6.81	23.20	62.69	2.81
Black oak bark extract..	51.11	0.86	23.86	24.17	3.00
Quercitron bark extract...	46.08	3.44	22.22	28.26	2.46
Bengal cutch extract......	62.64	2.66	8.09	26.61	1.48
Camel cutch.............	23.77	3.06	18.63	54.54	5.49

TABLE II—ELECTROPHORESIS OF CUBE GAMBIER

4 g. dry gambier extract per 100 cc.; both electrodes set at 5-cm. mark

Levels of Gambier Solution			
Left Limb	Right Limb		
Anode Cm.	Cathode Cm.	Time Min.	Displacement Cm.
7.8	8.0	0	Up 0.2
7.6	8.35	20	Down 0.35
			Av. 0.275 in 1200 sec.

Average voltage through 19.9 cm. = 114.3
∴ Potential gradient = 5.74 volts per cm.
P. D. = −0.005 volt[1]

[1] Negative because particles migrated to anode.

TABLE III—ELECTROPHORESIS OF QUEBRACHO

4 g. dry quebracho per 250 cc.; both electrodes at 5-cm. mark

Levels of Quebracho Solution			
Left Limb	Right Limb		
Anode Cm.	Cathode Cm.	Time Min.	Displacement Cm.
7.8	7.75	0	Up 1.40
6.4	9.1	20	Down 1.35
			Av. 1.37 in 1200 sec.

Average voltage through 19.9 cm. = 116.2
∴ Potential gradient = 5.83 volts per cm.
P. D. = −0.028 volt

It will be noted in the electrophoresis of gambier that the displacement downward at the negative pole was greater than the upward movement toward the positive pole. This phenomenon is noted in the electrophoresis of all colloids. Burton referred to this effect in the electrophoresis of inorganic colloids as the "settling of the colloid." It is an error, however, that cannot be lightly turned aside. Unpublished results from this laboratory on the electrophoresis of iron oxide hydrosols show a downward displacement as much as

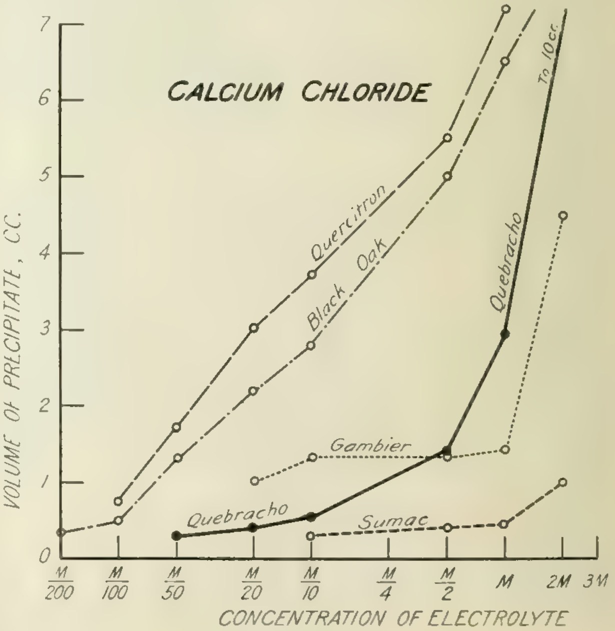

FIG. 2

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[8] *Phil. Mag.*, **1888**, 60.

[9] *Ibid.*, **11** (1906), 425, 472.

[10] THIS JOURNAL, **12** (1920), 465.

five to ten times as great as the upward displacement, depending on the concentration of the hydrosol. It is evident that this effect throws great doubt upon all the absolute values of electrical charge of colloids that are found in the literature. In a recent article, Burton[11] promises an investigation of this "settling," which he attributes to the action of gravity accelerating the downward electrophoresis and retarding the upward movement.

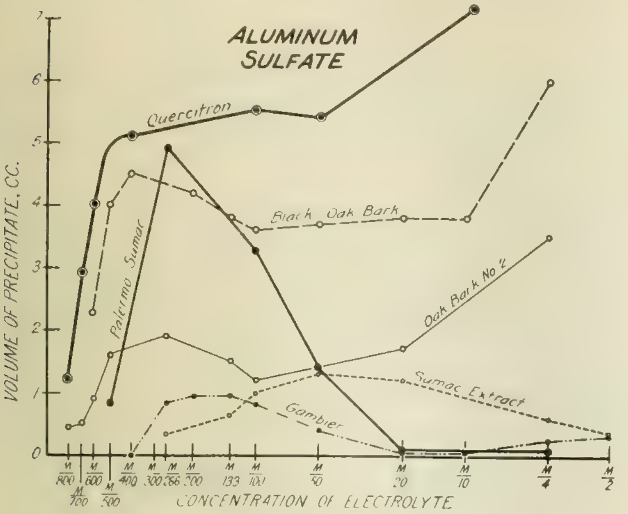

FIG. 3

The slightly greater upward movement noted in the particular quebracho experiment recorded was obtained with a number of extracts, and is probably due to a reprecipitation at the anode of some of the constituents of the liquor which were dissolved by the cathodic reaction in that limb of the U-tube during the preliminary 5-min. passage of the current in the reverse direction.

As a result of the effects of oxidation and reduction, as well as of formation of acid and alkali in the cathode and anode limbs, with the resulting dissolution and reprecipitation of some of the constituents of the tanning extract solutions, it was not always easy to tell just what was the electrophoresis displacement. The authors were obliged to make many preliminary experiments before they felt that they had one whose value they would care to publish. The behavior was not alike for any two extracts.

It is evident that the values which are given below for the electrical charges of the tannin particles are not absolutely correct. They are, however, not much more doubtful than the many published values obtained by electrophoresis. The authors do not attempt to calculate the values of the electrical charges per colloidal particle because such calculation involves the sizes of the particles. It is impossible to determine the sizes of colloidal particles by any method known at the present time and we are obliged to be content with values for the potential difference of the Helmholtz double layer only. The authors wish to emphasize the point that the published values for absolute electrical charges on colloidal particles are worthless, on account of the lack of a means for measurement of the sizes of colloidal particles.

RELATION BETWEEN P. D. AND ORDER OF CONDUCTIVITIES—The values obtained for the potential differences of the particles against the aqueous phase are listed in Table IV, together with the order of the conductivities. All the extracts showed anodic migration. The concentration in all the solutions was such as to give 1 per cent tannin, which meant about 4 g. total solids per 100 cc., except in cases of quebracho (2 g. per 125 cc.) and osage orange (1.6 g. per 100 cc.).

TABLE IV—POTENTIAL DIFFERENCES AND ORDER OF CONDUCTIVITIES

Increasing Potential Difference	Volt	Decreasing Conductivity
Gambier (cube)	−0.005	Sumac
Oak bark 2	−0.009	Gambier
Chestnut wood	−0.009	Oak bark
Hemlock bark (Wis.)	−0.010	Larch bark
Sumac	−0.014	Hemlock bark
Larch bark	−0.018	Chestnut wood
Osage orange	−0.018 (?)	Osage orange
Quebracho	−0.028	Quebracho

The value for osage orange is the only one concerning which there is any great uncertainty.

According to the theory that the combination of tannin with hide substance is a function of the electrical charge of the particles, the most drastically acting extract would be quebracho, and the mildest would be gambier, according to the above values of the P. D.

By comparison with the conductivity series, it is evident that while, in general, the more highly conducting extracts have the lower P. D. values, there are exceptions to this rule, so that it is apparent that the magnitude of the electrical charge is a function of the kind as well as the amount of nontannins present, as is to be expected.

TABLE V—P. D. OF QUEBRACHO EXTRACT

CONCENTRATION G. Dry Solids in 250 cc	P. D. Volt
8	−0.024
4	−0.028
2	−0.029
1	−0.030

RELATION BETWEEN P. D. AND CONCENTRATION—The results obtained upon measuring the P. D. of a quebracho extract at different concentrations are assembled in Table V.

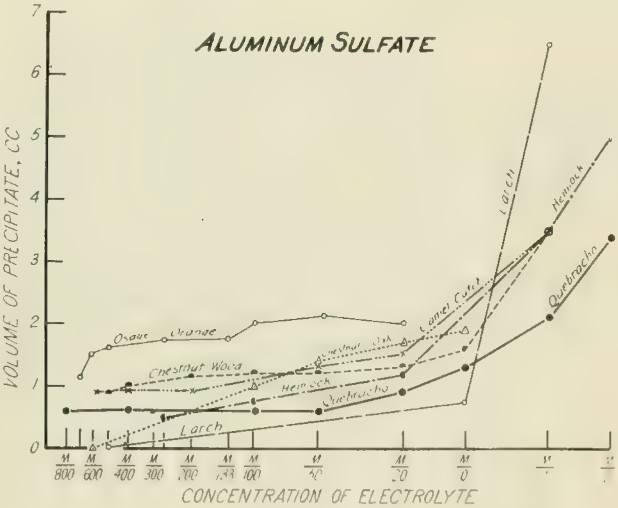

FIG. 4

The P. D. increases upon dilution of the extract, as is to be expected according to the "complex theory" of colloids, since dilution decreases the concentration of electrolyte in the outer layer surrounding the particle and permits greater ionization of the peptizing electrolyte adsorbed on the particle.

RELATION BETWEEN P. D. AND ACIDITY—Since the negative charge on a colloid is readily increased by the addition of hydrogen ion, such addition ought to lower the P. D. of a vegetable tanning extract. The data in Table VI show that this is true.

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[11] *Proc. Roy. Soc. London*, **95A** (1919), 480.

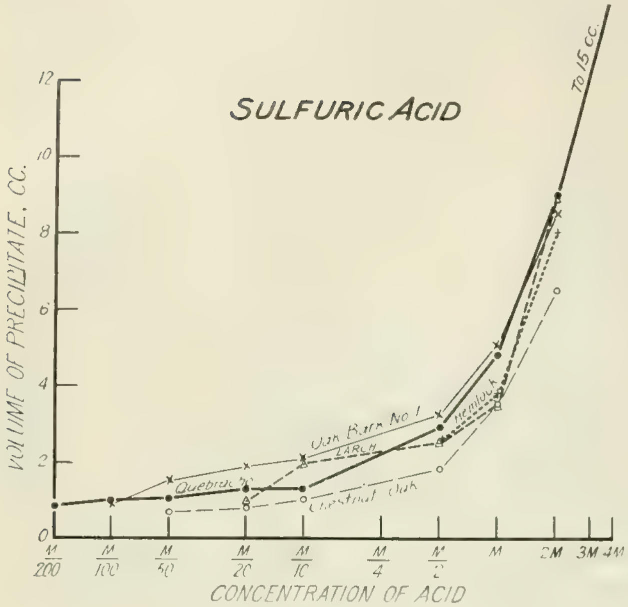

FIG. 5

TABLE VI—EFFECT OF ADDITION OF ACID

4 g. dry quebracho extract per 250 cc.

0.1 N HCl added per 100 Cc. Cc.	P. D. Volt
0	−0.024
1	−0.014
1.5	−0.010
2.0	Approx. 0

EFFECT OF DIALYSIS—On the other hand, dialysis of extracts ought to raise the P. D., as a result of the removal of nontannins from the solution. Table VII describes the results obtained by dialysis through collodion sacs against distilled water.

TABLE VII—EFFECT OF DIALYSIS

		Dialysis		
MATERIAL	Concentration G. per 250 Cc.	Time Hrs.	Volume Increase to Cc.	P. D. Volt
Quebracho	4	60	415	−0.033
Osage orange[1]	4	24	370	−0.024
Sumac	4	24	460	−0.026
Cube gambier	8.2	24	390	−0.029
Hemlock bark	...	24	...	−0.024

[1] A 200-cc. portion of this solution, again dialyzed for 24 hrs., increased to 240 cc. P. D. = −0.036 volt.

In all cases the P. D. increased as was expected. It is true that part of the increase in P. D., is attributable to the dilution of the solution, but the removal of the nontannins also was a contributing factor.

PRECIPITATION OF VEGETABLE TANNING EXTRACTS

The action of vegetable tanning extracts toward electrolytes should throw some light upon their colloidal nature. With this idea in mind many extracts were treated with various electrolytes in different concentrations and the volumes of precipitated material were measured.

TECHNIC

Aqueous dispersions or solutions of the extracts were made up so that 100 cc. of solution contained 4 g. of total solids. Before adjusting to the mark, the solutions were kept at 85° C., and cooled to 25° C. before adjusting to volume. The stock solution was then centrifuged for 5 min. at about 1000 "times gravity" in order to throw down coarse suspended matter.

Twenty-five-cc. portions were placed in 100-cc. graduated "oil tubes" (tubes tapering to a conical end). Equal volumes of electrolyte solutions of varying concentration were poured into each tube, allowed to stand for 15 to 30 min., since precipitation was not always instantaneous, and finally centrifuged for 5 min. at 1000 "times gravity." The volumes of the precipitates were plotted against the concentrations of electrolyte employed.

RESULTS

The results may be most conveniently studied by grouping them under the various electrolytes used. Each available extract was not tested with all electrolytes since in some cases preliminary experiments indicated that further work would be fruitless.

MONOVALENT CATION. *Potassium Chloride*—Concentrations of potassium chloride from 0.02 *M* to 4 *M* gave only negligible amounts of precipitate with gambier and quebracho. Oak bark gave a gradually increasing salting out effect. Since gambier and quebracho represent extreme types of tans no further tests were made with this salt.

Hydrochloric Acid—Concentrations from 0.01 *M* to 6 *M* were used. Gambier and quebracho showed appreciable amounts of precipitate only at the highest concentration of the acid and since this was not a simple colloid precipitation, no further experiments were attempted. (Fig. 6.)

Sulfuric Acid—Quebracho, hemlock, oak bark, chestnut oak, and gambier gave progressively increasing amounts of precipitate (salting out) with concentrations of acid from 0.005 *M* to 4 *M*. (Fig. 5.) No precipitate was obtained with sumac until molal acid was reached. Acid of this concentration threw down gummy masses, similar to those obtained with aluminium sulfate. At 4 *M* concentration a flocculent precipitate was formed.

Phosphoric Acid—Gambier began to give an appreciable precipitate only at 4 to 7 *M* concentration. With sumac a gummy mass was thrown out at 2 *M*, as was observed in the case of sulfuric acid and aluminium sulfate, and at 4 *M* to 7 *M* a flocculent precipitate formed which left the supernatant solution almost colorless. A salting out effect was obtained with quebracho. (Fig. 6.)

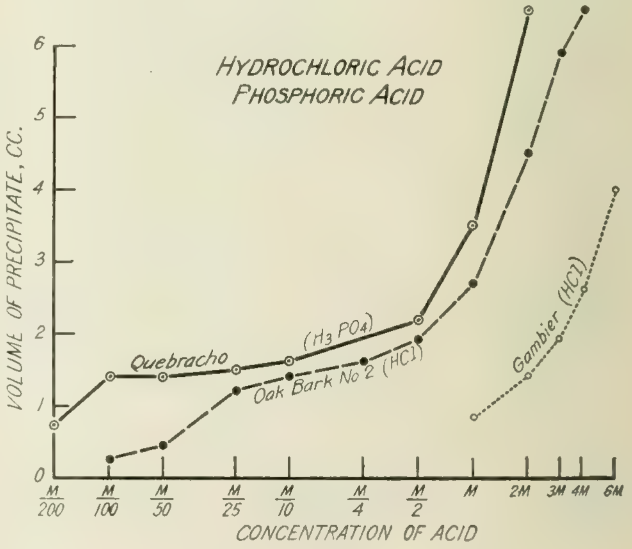

FIG. 6

Acetic Acid—Experiments with quebracho, sumac, gambier, and oak bark were run with concentrations of acid from 0.005 *M* to 4 *M*. There was no appreciable precipitation in any case. It is of interest to note that at the higher concentrations the suspended matter began to dissolve or peptize.

Formic Acid—Concentrations from 0.005 *M* to 12.5 *M* were used. Sumac, chestnut oak, hemlock, gambier, larch bark and oak bark gave no precipitation up to 4 *M*. The suspended matter began to dissolve or peptize at 4 *M*. Quebracho and quercitron were precipitated, but the precipitate dissolved at 2 *M* to 4 *M*. (Fig. 7.)

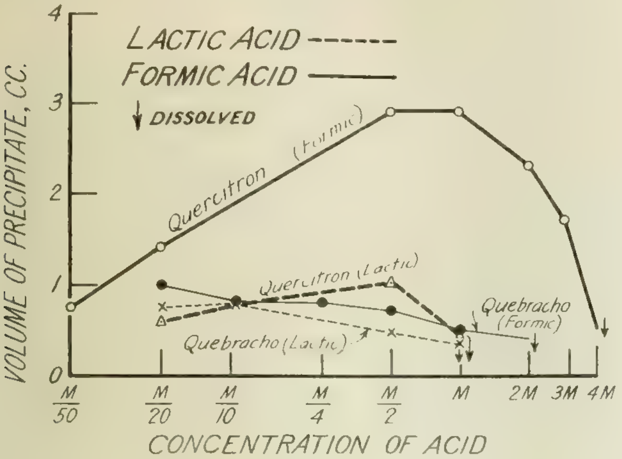

Fig. 7

Lactic Acid—Concentrations from 0.005 *M* to 2 *M* were employed. The effects of this acid were similar in kind, but not in degree, to those with formic acid. (Fig. 7.) The precipitates with quercitron and quebracho redissolved at lower concentrations of lactic acid than of formic acid. Since lactic is the weaker acid, and also since this redissolving was not found with hydrochloric or with sulfuric acids, the phenomenon must be due to chemical properties other than concentration of hydrogen ion.

DIVALENT CATIONS. *Barium Chloride*—On account of limitations of solubility, this salt was employed up to a final concentration of 0.5 *M*. Progressive salting out occurred with oak bark, chestnut wood, quebracho, gambier, and hemlock. (Fig. 1.)

Calcium Chloride—Final concentration of 2 *M* was possible with this salt. As with barium chloride, increasing amounts of precipitate were obtained with quercitron, black oak, quebracho, gambier, and sumac. At the same concentration of these salts the different extracts gave in some cases less, and in others more, precipitate, showing the presence of substances reacting with barium and calcium ions to form chemical compounds of different solubilities. (Fig. 2.)

TRIVALENT CATION. *Aluminium Sulfate*—In the precipitation of negatively charged colloidal dispersions, aluminium sulfate is not only a powerful precipitant, but it also gives the "irregular series" or "tolerance zone" which is typical of the action of weak base cation, strong acid anion salts, as shown by Buxton and Teague,[12] and by Freundlich and Schucht.[13]

The concentrations of aluminium sulfate used ranged from 0.00125 *M* to 0.5 *M*.

The "irregular series" effect was obtained with the following extracts: gambier, sumac, Palermo sumac, oak bark No. 2, black oak bark, and not so markedly with quercitron. Precipitation set in generally at 0.00125 *M* concentration of the salt, rose rapidly to a maximum, dropped off into a "tolerance zone," and then started upward again. (Fig. 3.)

Those which gave no "irregular series," at least up to 0.5 *M* concentration of the salt, were: Osage orange, chestnut wood, chestnut oak, hemlock bark, larch bark, quebracho and camel cutch. They began to precipitate at 0.00125 *M*, rising gradually to about 0.1 *M* where there was an abrupt upward trend similar to a salting-out effect. These extracts are not so sensitive to precipitation by aluminium sulfate as the first mentioned.

Bengal cutch is in a separate category, since it was unaffected by the addition of aluminium sulfate.

Interpretation of Results

The interpretation of the effects of the several electrolytes is masked by the salting out and chemical precipitation of the molecularly dispersed substances present in addition to the colloidal tannins. The writers had hoped that the order of sensitiveness to precipitation by mono-, di-, and trivalent cations would help show the order of magnitude of the potential differences of the particles against the aqueous phase, but the interference by the large amounts of molecular dispersions of nontannins in salting out spoiled this anticipation. The presence of this salted-out, molecularly dispersed material was shown in several cases where the coagula caused by the calcium and aluminium salts were found to redissolve to a large extent upon addition of water. If it were all gel substance it should not be reversible.

The conduct of the extracts shows that there is a large amount of colloidal matter present, that it belongs to a type of dispersion with properties between the intermediate and hydrophilic dispersions, and, hence, that the measurements reported in the first part of the paper are justified.

From the colloidal point of view, vegetable tanning extracts constitute an unexplored field, and the authors believe that the precipitation graphs included in this article will prove of value when interpreted in the light of further research.

Acknowledgment

We take pleasure in expressing our indebtedness to Messrs. A. F. Gallun and Sons Co., of Milwaukee, for grants in aid of this investigation.

National Safety Council Census

It is known that the chemical industry, because of its inherent hazards, has always been among the leaders in industrial safety, but it has never been definitely established how many persons in the chemical industry are engaged in accident prevention and industrial health work. The National Safety Council is now taking a census of safety men in the chemical industry, as well as in all other industries and in public safety work.

When this census is completed it will give a good indication of the extent of such work in chemical plants all over the country, and will afford the first basis of comparison with similar work in other industries. The census will include not only members and employees of members of the National Safety Council, but all other persons engaged in safety and industrial health activities. Most of the principal chemical plants are members of the Council. The headquarters of the Council are at 168 N. Michigan Ave., Chicago, Ill.

Associated Technical Societies of Detroit

The Associated Technical Societies of Detroit, an affiliation of the architectural, engineering, and other technical societies of the city, has just been organized. The Detroit Section of the American Chemical Society is one of the members of the association.

The paramount use of the association to its members and to the public is its opportunity for public service for the city and for the state of Michigan. It will take an active interest in all matters where engineering, architecture, or technical subjects are of importance. The council will assist in furnishing definite and accurate information to the public. The association will offer its assistance and advice to city and state officials whenever required. The purpose of the association's activities is to provide the most reliable technical information for the proper consideration of public improvements and public undertakings

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[12] *Z. physik. Chem.*, **57** (1907), 76.

[13] *Ibid.*, **85** (1913), 641.

Determination of True Free Sulfur and True Coefficient of Vulcanization in Vulcanized Rubber—II[1]

By W. J. Kelly[2]

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The following paper describes methods of analysis by means of which a more complete study of the distribution of sulfur between the various ingredients of a rubber compound can be made. New light will also be thrown on the mechanism of vulcanization and acceleration. It is freely admitted that alcoholic potash and ether-hydrochloric acid have been long known as reagents in rubber analysis, but their application to the separation of the different forms of sulfur, except metallic sulfides, is entirely new.

If carried to their ultimate possibilities, including the use of other extraction media, these methods should be of considerable help in elucidating the theories of vulcanization.

In a previous paper,[3] it was shown that the sulfur present in vulcanized pure gum stocks could be divided into four parts as follows:

- A—Sulfur soluble in acetone:
  - (1) True free sulfur
  - (2) Combined with resins and proteins
- B—Sulfur insoluble in acetone:
  - (1) Combined with rubber
  - (2) Combined with resins and proteins

It is at once evident that this classification applies only to pure gum stocks and that if compounded stocks are analyzed there will be more classes in B, while A will remain the same. If basic inorganic substances such as ZnO and PbO are present there is always some metallic sulfide formed. All the organic accelerators react with sulfur during the cure, giving rise to new bodies which may or may not be soluble in acetone.

The acetone-soluble compounds will not interfere in any way with the procedure described in the previous paper, but in the case of the insoluble part an amplified classification is necessary. The following outline will account for all of the sulfur in compounded stocks with the exception of those containing insoluble sulfates, such as those of barium, calcium, or lead.

- A—Soluble in acetone:
  - (1) True free sulfur
  - (2) Combined with resins, proteins, and accelerators
- B—Insoluble in acetone:
  - (1) Combined with rubber
  - (2) Combined with resins, proteins, and accelerators
  - (3) As metallic sulfides

It is evident that the acetone-insoluble sulfur combined with resins, proteins, and accelerators may be subdivided according to the means employed for its removal from the rubber. Treatment with alcoholic potassium hydroxide will remove at least part of the resin compounds and also render the proteins soluble by hydrolysis. The accelerators and compounds formed from them during the cure will also be more or less affected by the alcoholic potash, and especially by the ether-hydrochloric acid which is used to evolve hydrogen sulfide from the metallic sulfides. According to Bedford and Scott[4] and Bruni and Romani,[5] the accelerators form mercapto and polysulfide compounds during the cure. These will all be decomposed or rendered soluble by the alcoholic potash and ether-hydrochloric acid treatments, and the sulfur which they contain will be removed. Hence sulfur combined with resins, proteins, and accelerators may be divided into two parts, one of which is soluble in alcoholic potash and the other in ether-hydrochloric acid.

The analytical methods for the separation of these classes of sulfur are the subject of this paper.

Previous to the development of the alcoholic potash treatment, an attempt was made to remove sulfur insoluble in acetone and not combined with the rubber by dissolving the acetone-extracted sample in xylene and filtering off the insoluble part. The sulfur compounds remaining on the filter were oxidized and their sulfur content determined. Three analyses on a stock which yielded 0.34 per cent sulfur upon the alcoholic potash treatment gave 0.074, 0.085, and 0.053 per cent of sulfur insoluble in acetone and xylene. It is entirely possible that the compounds of resins and sulfur may dissolve in xylene and pass through the filter. The protein products may be insoluble, but the difficulty of obtaining a clean separation by this method is too great for ordinary use. It was therefore abandoned for the alcoholic potash method, which extracted a larger amount of sulfur and gave more concordant and dependable results.

ANALYTICAL PROCEDURE

METHODS OF OXIDATION—The method proposed by Kratz, Flower and Coolidge[6] gave the best results, especially with rubbers containing large amounts of organic matter. The sample was oxidized with a mixture of nitric acid and zinc nitrate, followed by bromine and potassium chlorate, and the solution was evaporated and baked. This method was used in the determination of total and combined sulfur. The free sulfur, total acetone-insoluble sulfur, and ether-hydrochloric acid-soluble sulfur were oxidized with fuming nitric acid-bromine mixture. The hydrogen sulfide evolved by ether-hydrochloric acid was collected and oxidized in potassium bromide-bromine solution, and the oxidation was completed with nitric acid. The alcoholic potash extract was oxidized, first with potassium bromide-bromine, then with nitric acid, in order to avoid adding the acid to solid potassium hydroxide.

OXIDIZING SOLUTIONS—Nitric acid-zinc nitrate was made up by dissolving 16 g. of C. P. zinc in concentrated nitric acid and diluting to 100 cc. with the acid.

Fuming nitric acid was saturated with liquid bromine by shaking the two together.

The potassium bromide-bromine solution contained 12 g. of bromide and 16 g. of bromine per 100 cc.

TOTAL SULFUR—A 0.5-g. sample was treated with 20 to 25 cc. of nitric acid-zinc nitrate solution, care being taken that the sample was kept cool until it was all dissolved; otherwise it was likely to catch fire. Ten cc. of the fuming nitric acid-bromine mixture were added to the solution, which was heated till all the bromine was evolved. About 0.5 g. of potassium chlorate was then added and the solution was evaporated to dryness. The flask was then heated to a dull red heat over a free flame, until the zinc nitrate had entirely decomposed and all the organic matter had oxidized.

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[1] Presented before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Research Chemist.

[3] This Journal, **12** (1920), 875.

[4] *Ibid.*, **13** (1921), 125.

[5] *India Rubber J.*, **62** (1921), 63.

[6] *India Rubber World*, **61** (1920), 356.

After cooling the flask, its contents were dissolved in hydrochloric acid and diluted, and the sulfur was precipitated and weighed as barium sulfate.

ACETONE-SOLUBLE. *Total*—A 0.5–1.0-g. sample was extracted over night with acetone and the solvent evaporated. The entire residue was oxidized with nitric acid-bromine mixture, followed by potassium chlorate. The solution was evaporated twice with a few cc. of hydrochloric acid to remove the nitric acid, dissolved in hydrochloric acid, filtered if necessary, and the sulfur precipitated and weighed as barium sulfate.

True Free Sulfur—Another 0.5–1.0-g. sample was extracted with acetone and the solvent distilled off until only about 5 cc. were left. The residue was evaporated in an oven at a temperature not exceeding 60° C. The true free sulfur was separated from the organic material present by treatment with alcohol saturated with sulfur, as described in the earlier paper.

The difference between the two determinations gave the organically combined, acetone-soluble sulfur.

ACETONE-INSOLUBLE SULFUR. *Total*—This was determined on a sample previously extracted with acetone. The oxidation and precipitation were carried out in exactly the same way as for total sulfur.

Sulfur Combined with Resins, Etc., Soluble in Alcoholic Potash—The sample previously extracted with acetone was boiled for 8 hrs. in a 5 per cent alcoholic potash solution, after which the solution was poured off and the rubber washed three or four times with alcohol. It was next extracted over night in an underwriter's apparatus with 95 per cent alcohol, in order to remove all the alkaline solution. The two solutions were combined and evaporated, and the residue was oxidized with 10 cc. of potassium bromide-bromine solution, followed by nitric acid. After the removal of any silica produced by the action of the potash on the glass, the sulfur was precipitated as barium sulfate.

Metallic Sulfide—The method used to evolve hydrogen sulfide from the metallic sulfides present was a modification of that proposed by Stevens,[7] who treated the sample with a mixture of aqueous hydrochloric acid and ether. Owing to the fact that ether penetrated very rapidly into the rubber, a solution of dry hydrochloric acid in ether was used. After extraction with acetone and alcoholic potash, the sample was treated with 50 cc. of ether-hydrochloric acid in a flask fitted with a separatory funnel and a delivery tube, and the hydrogen sulfide evolved was collected in potassium bromide-bromine solution. The last traces of hydrogen sulfide were removed by distilling over about half the ether. The bromide-bromine solution was treated with nitric acid, and the sulfur precipitated and weighed as barium sulfate.

Combined with Accelerators, Etc., Soluble in Ether-HCl—The sample which had been treated with ether-hydrochloric acid was washed several times with ether, and the solvent was evaporated. The residue was oxidized with nitric acid-bromine and the sulfur determined as barium sulfate.

Combined with Rubber—The sample which had been extracted successively with acetone, alcoholic potash, and ether-hydrochloric acid was finally treated exactly as described for the total sulfur.

EXPERIMENTAL RESULTS

In order to test these methods, seven stocks were mixed, cured, and analyzed. The results are given in Table I. In some cases it will be noted that the total sulfur determined does not check with that calculated from the formula. As the results of the single determinations all checked very well, the discrepancy is probably due to an error in weighing out or in mixing the batch. All of the figures are the averages of at least two analyses and the checks obtained were all within 0.03 to 0.04 per cent calculated on the total stock.

TABLE I

	Stock Number 1	2	3	4	5	6	7
Composition							
Pale crepe	100	100	100	100	100	100	100
Zinc oxide	25	..	10	..	15	15	15
Sulfur	8	5	6	6	5	5	5
Hexamethylenetetramine	..	..	..	..	1	1	1
Thiocarbanilide	..	2	2	..	..	..	..
Litharge	..	..	..	10	..	..	..
Glue	..	..	..	..	..	5	..
Gas black	..	..	..	..	..	..	10
Cure							
Time, minutes	105	90	25	30	60	60	60
Temperature, ° C	141	141	141	141	141	141	141
Percentage of Sulfur							
Total sulfur:							
Calculated	6.02	4.94	5.32	5.17	4.13	3.97	3.82
Determined	6.19	4.88	5.43	5.19	4.14	3.96	3.81
Total acetone-soluble sulfur	4.47	3.30	4.24	2.35	2.42	2.18	1.96
True free sulfur	4.03	3.18	3.95	2.28	2.12	2.06	1.80
Sulfur combined with resins (by diff.)	0.44	0.12	0.29	0.07	0.30	0.12	0.16
Acetone-insoluble sulfur:							
(1) Sol. in alc. KOH	0.17	0.13	0.06	0.26	0.06	0.17	0.11
(2) Sol. in ether-HCl	....	0.12	0.17	....	0.21	0.04	0.25
(3) Sulfide sulfur	0.17	0.00	0.20	0.72	0.19	0.47	0.25
(4) Combined with rubber	1.42	1.38	0.84	1.82	1.30	1.03	1.19
TOTAL 1, 2, 3, 4	1.76	1.63	1.27	2.80	1.76	1.71	1.80
TOTAL ACETONE-INSOLUBLE SULFUR (DETERMINED)	1.73	1.59	1.20	2.85	1.75	1.74	1.85

DISCUSSION OF RESULTS

The results obtained show beyond doubt that there is, in the acetone extract, a considerable amount of sulfur which is combined with organic matter. This sulfur is not available for further vulcanization as such, but in the light of Bedford and Scott's work the compounds thus formed may very well be a part of the natural accelerator of the rubber.

The classification of acetone-insoluble sulfur into four parts is susceptible of expansion, for in the case of some of the accelerators it is not at all certain that their sulfur reaction products can be entirely removed by the methods described. It is certain, however, that a large amount of sulfur, heretofore considered as combined with the rubber, has been removed by means which leave no doubt as to the fact that it was not combined with the rubber.

It is of course well known that both alcoholic potash and ether-hydrochloric acid have been used before in rubber analysis, but the analysis of the extracts for sulfur has not been made.

No series of cures have been analyzed according to these methods, but their value as a means of throwing light on the mechanism of vulcanization can be estimated by the following example:

Two stocks containing about the same amount of sulfur, one with zinc oxide and one without, were cured for 1 hr. 45 min. at 141° C. The analyses are listed in Table II, all figures being based on 100 parts of rubber.

TABLE II

I—PALE CREPE 100, SULFUR 7.5; II—PALE CREPE 100, ZnO 25, SULFUR, 8

SULFUR	I	II
True free	5.04	5.37
Acetone-soluble	0.20	0.59
Soluble in alcoholic KOH	0.08	0.23
As ZnS	0.00	0.23
Combined with rubber	2.14	1.89
TOTAL	7.46	8.31

The values for total sulfur check quite well with the amount added. In Sample 2 the discrepancy may be due either to an error in weighing or to sulfur in the zinc oxide used.

It will be seen that the amount of sulfur combined with the rubber in Sample 2 is less than that in Sample 1 in spite of the fact that there was more sulfur present in Sample 2. This shows that the zinc oxide holds back the reaction between rubber and sulfur to a marked degree.

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[7] *Analyst*, **40** (1915), 275.

Alleged Adsorption of Alumina from Aluminium Sulfate Solutions by Cellulose[1]

By Alfred Tingle[2]

THE E. B. EDDY CO. LTD., HULL, P. Q.

THE work here described was undertaken with the object of obtaining some first-hand information as to the extent to which alumina is adsorbed from its sulfate solution by cellulose in general and paper-making pulps in particular. The occurrence of this phenomenon is asserted or assumed by many writers, but the evidence on which these assertions are made is seldom cited.

Adsorption of alumina by cellulose is appealed to by Cross and Bevan, for example, as a factor of importance in the theory of paper sizing.[3] The only reference in original literature which the present writer has been able to find is to the work of Schwalb and Robsahm[4] and of Sutermeister.[5] The phenomena observed by Schwalb and Robsahm were obviously not connected with adsorption at all, but were simple precipitations of alumina by the noncellulose constituents of the pulp. Sutermeister found much lower figures for the amount of $Al_2(SO_4)_3$ decomposed, but the origin of the phenomena observed remains a little obscure. More lately Kolthoff,[6] using purified filter paper, has concluded that positive ions are separated from salts not by cellulose, but by the ash constituents.

Expts. 2 and 3, described in detail below, show that neither acid-washed filter paper nor well-washed bleached sulfite pulp removes any analytically appreciable amount of alumina from a basic solution of aluminium sulfate, when brought in ordinary contact therewith. Expt. 3 shows that pure filter paper does not adsorb alumina from a nonbasic solution of sulfate even when the two are very thoroughly beaten together, while Expt. 4 shows conditions under which a retention of alumina may occur. In this case the pulp used had an alkaline reaction. Some precipitation took place (shown by the reduced amount of "total Al_2O_3"), while the still greater reduction in the combined alumina present indicated the formation of a "basic salt," but these changes were obviously due to chemical action, not to adsorption or any related phenomenon. Expt. 5 serves to show that even when a neutral solution of aluminium sulfate is converted into a basic one in the presence of a *well-washed* sulfite pulp, the cellulose adsorbs no alumina.

Some errors on the subject may well have arisen from manipulative mistakes. It is sometimes forgotten that dilution of a basic aluminium sulfate solution will cause the precipitation of alumina, so that apparent failures to wash aluminium salts completely out of cellulose must not be taken as conclusive evidence of adsorption till all surrounding factors have been very carefully scrutinized.

The present work is not regarded by the author as justification for drawing a final conclusion, but as establishing grounds for reasonable doubt as to whether the alleged adsorption actually takes place. It makes it reasonable for the matter, which has a very practical bearing if the theory of paper sizing is ever to be put on its feet, to be investigated further in an authoritative manner when the supply of pure cellulose which has been promised to the Cellulose Section of the SOCIETY is available for research purposes.

ANALYTICAL METHODS

"COMBINED Al_2O_3"—Either Method A or Method B,[7] described previously, was used. Whichever method was chosen as more convenient was adhered to throughout the same set of determinations.

"TOTAL Al_2O_3"—The method was that of W. Blum.[8]

"BASIC Al_2O_3"—When not found by difference between "total" and "combined" Al_2O_3, the Craig-Scott method[9] was used with a slight modification of no importance.

PREPARATION OF STRONGLY BASIC ALUMINIUM SULFATE SOLUTIONS

To 300 cc. of a 10 per cent solution of pure $Al_2(SO_4)_3$, 100 cc. of 4 per cent NaOH solution were added. The resulting precipitate was well stirred and poured into another 300 cc. of the same $Al_2(SO_4)_3$ solution. After a few hours the mixture was filtered. The filtrate was diluted for use as required, but when so diluted could not be preserved for long without change.

DESCRIPTION OF EXPERIMENTS

EXPT. 1—Approximately 6 g. (dry weight) of well washed and beaten, bleached sulfite spruce pulp, in a 500-cc. graduated flask, were treated with 100 cc. of a basic aluminium sulfate solution. The mixture was agitated, diluted to 500 cc., and filtered. A blank experiment was made at the same time by diluting 100 cc. of the same basic sulfate solution to 500 cc. with water, and filtering.

"Basic Al_2O_3" was determined in 100 cc. of each filtrate, with the following results:

	PULP PRESENT	BLANK
NaOH equivalent to "Basic Al_2O_3," cc.	24.1	24.0
Titer of NaOH	0.27 *N*	0.27 *N*
"Basic Al_2O_3" in 100 cc. filtrate, grams	0.1140	0.1135

EXPT. 2—A filter was prepared by folding together 15 No. 30 Whatman 15-cm. filter papers (total weight approx. 20 g.), and 100 cc. of a clear, rather strong solution of basic aluminium sulfate were poured thereon. Only 55 cc. of filtrate passed through, the remainder being absorbed by the papers. Determinations were made as follows on 50 cc. of the original solution and on the same volume of filtrate:

	Original Solution Grams	Solution Passed through Filter Grams
Total Al_2O_3	0.1287	0.1291
"Combined Al_2O_3"	0.1018	Not determined
"Basic Al_2O_3" (by difference)	0.0265	Not determined

EXPT. 3—Twenty-two Whatman No. 44 9-cm. filter papers (approx. weight 10 g.) were beaten in a ball mill for 2 hrs. with 200 cc. of $Al_2(SO_4)_3$ solution (containing no "basic Al_2O_3") and 400 g. of pebbles. The resulting pulp was pressed and filtered. The total Al_2O_3 found in 100 cc. of the original solution was 0.1620 g.; in 100 cc. of the filtrate, 0.1619 g. A microscopic examination of the fibers before and after the beating indicated that a considerably increased degree of hydration had been induced during the process.

EXPT. 4—About 20 g. of air-dry, bleached sulfite spruce pulp, washed only by an ordinary mill process, were beaten in a ball mill with 400 cc. of aluminium sulfate solution under the conditions of Expt. 3. The solution was then filtered from the pulp. Determinations were made on this filtrate and on the original solution, as follows:

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[1] Presented before the Section of Cellulose Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Chemist to the E. B. Eddy Co. Ltd.

[3] "Paper Making," 5th ed., 248.

[4] *Wochbl. Papierfabr.*, **43** (1912), 1454.

[5] *Pulp Paper Mag. Can.*, **11** (1913), 803.

[6] *Pharm. Weekblad.*, **57** (1920), 1510, 1529.

[7] THIS JOURNAL, **13** (1921), 420.

[8] *J. Am. Chem. Soc.*, **38** (1916), 1282.

[9] THIS JOURNAL, **7** (1915), 1059.

	Total Al_2O_3 in 100 Cc. Grams	"Combined Al_2O_3" in 100 Cc. (Determined on 20 cc.) Grams	"Basic Al_2O_3" in 100 Cc. by Difference Grams
Original solution	0.1809	0.1807	0.0002
Solution after beating and filtration	0.1793	0.1783	0.0010
Change	−0.0016	−0.0024	+0.0008

The solution which had been in contact with the pulp gave a slight precipitate with $(NH_4)_2C_2O_4$ after precipitation of the Al_2O_3.

An aqueous extract made from another sample of the same pulp was alkaline to methyl red, and gave a precipitate when boiled with a dilute solution of $Al_2(SO_4)_3$.

EXPT. 5—Approximately 6 g. of well washed and beaten sulfite spruce pulp were introduced into a 500-cc. graduated flask. To this were added 200 cc. of "white rosin size" and the mixture was well agitated. While the agitation continued 100 cc. of $Al_2(SO_4)_3$ solution (approximately 10 per cent) were added. The contents of the flask were made up to 500 cc. and filtered.

A blank experiment was made in every respect similar but omitting the presence of pulp. Under these conditions it has been shown in the course of work not yet published that the aluminium resinates are hydrolyzed, the alumina remaining in solution as "soluble basic sulfate."

The "combined Al_2O_3" and "basic Al_2O_3" were determined in aliquot portions of the filtrate, 50 cc. being taken for the former and 100 cc. for the latter determination. Unfortunately a note of the titer of NaOH solution used in the determination of "basic Al_2O_3" has been lost, but as the same solution was used both for main experiment and blank, the results can still be compared, though not stated in weight of Al_2O_3.

"COMBINED Al_2O_3"

	NaOH Used 0.3246 *N* Cc.	"Combined Al_2O_3" in 50 Cc. Filtrate Grams
In presence of pulp	26.0	0.1438
In absence of pulp	25.9	0.1432

"BASIC Al_2O_3"

	NaOH Used for 100 Cc. Filtrate Cc.
In presence of pulp	26.0
In absence of pulp	26.1

The differences shown may therefore be considered as within reasonable experimental error.

CONCLUSIONS

1—The observed withdrawal of Al_2O_3 from solutions of $Al_2(SO_4)_3$ in the presence of cellulose is due to chemical precipitation by noncellulose material present as an impurity.

2—No adsorption of Al_2O_3 by cellulose of reasonable purity could be observed in such solutions, ordinary analytical methods being adopted. Basic and neutral solutions were both tried.

3—The question should be thoroughly investigated and an authoritative decision reached when pure standard cellulose becomes available for research.

4—Methods of investigation which depend on attempts to separate aluminium salts from cellulose by repeated washing can only be employed when great caution is used as to the nature of the materials. They can never be trusted when basic solutions are in question.

The Penetrability of Filter Paper[1]

By R. C. Griffin[2] and H. C. Parish

ARTHUR D. LITTLE, INC., CHARLES RIVER ROAD, CAMBRIDGE, MASSACHUSETTS

In the following paper the common methods of testing the penetrability of filter paper are discussed, and a new penetrability tester is described. Attention is called to the effect of temperature and time upon the speed of filtration of distilled water. Comparative penetrability figures are given for five representative grades of quantitative papers.

VARIOUS methods of testing the speed of filtration or the penetrability of filter paper have been proposed. The method probably in most common use is to fit a circle of the paper into a funnel and fill it with water or some other liquid. The speed of filtration is then either (1) judged arbitrarily, (2) measured by timing the flow of a definite volume of liquid through the paper, or (3) compared with some other paper as a standard, which is tested in the same way on a similar funnel.

Such a test, if properly carried out, will undoubtedly provide a "rough and ready" comparison between different filter papers. It is obvious, however, that there are numerous factors which will affect the results, principally: (1) the length and internal diameter of the stem of the funnel; (2) the angle of the funnel; (3) the way in which the paper is folded and fitted into the funnel; and (4) the amount of liquid filtered and the manner in which it is poured upon the filter. Obviously, therefore, very misleading conclusions may be reached by such a test. Furthermore, it does not furnish a ready means of obtaining figures that may be recorded for future comparisons.

Herzberg has designed an apparatus[3] (Fig. 1) which consists essentially of a vertical, cylindrical, glass water-reservoir with an air-tight cover through which passes the stem of a funnel nearly to the bottom. A stopcock in the cover allows the water pressure to be adjusted according to the volume of air above the water in the reservoir. Connected to the reservoir at the bottom, by means of a U-tube with a valve cock, is a cylindrical box, 5 cm. in diameter, to hold the paper. In operation the upper half of this box is taken off and the cock opened slowly until the water reaches the upper edge. The paper is then laid in position, the upper half of the box replaced, and the cock again opened until water issues in a regular stream. The water is collected in a 100-cc. volumetric flask and the time required to fill the flask is determined, under a definite head of water, usually 5 cm.

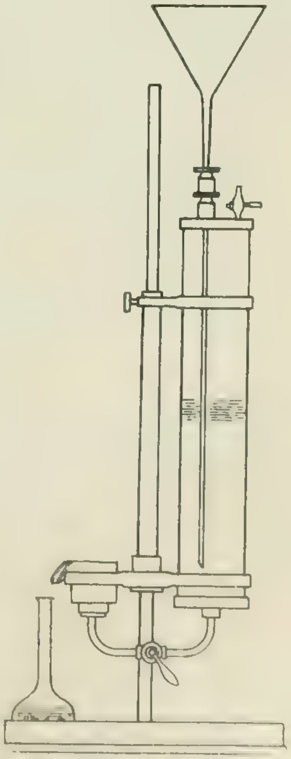

FIG. 1—HERZBERG'S PENETRABILITY TESTER

In attempting to use the Herzberg tester for routine control tests in filter paper manufacture the writers have found difficulty in getting consistent results. This was probably largely due to failure of the operator to maintain conditions

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[1] Received July 9, 1921.

[2] Director of Tests, Arthur D. Little, Inc.

[3] H. P. Stevens, "The Paper Mill Chemist," Scott, Greenwood & Son, London, 1919, 2nd ed., p. 267.

uniform, particularly as regards the water pressure. It is, of course, desirable to have any instrument which is to be used in routine control tests as nearly automatic as possible. With this in view there has been developed a penetrability tester which after many months' trial has been found to give consistent results. It is also of rugged construction, compact, and simple to manipulate.

Fig. 2 shows a horizontal and a vertical cross section of the tester. The entire apparatus, with the exception of the tube leading from the overflow cup to the base of the apparatus and the wire screen, is made of lead. The part carrying the overflow dam E and the wire screen D lifts off from the lower portion, both contact surfaces being planed. The distilled water supply enters the vertical tube at right angles at a point about 4 in. above D. This water supply is controlled by means of a stopcock. It is kept in any suitable form of reservoir and feeds by gravity.

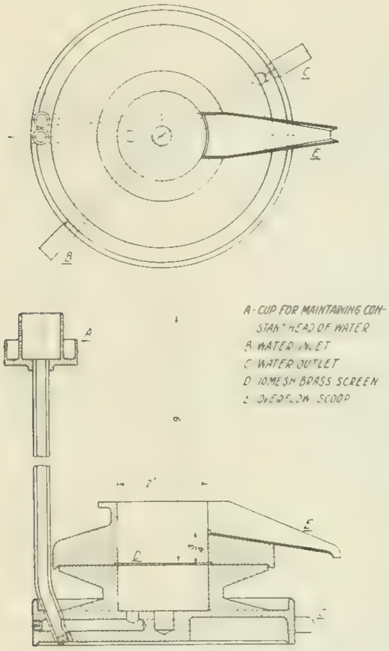

Fig. 2—Penetrability Tester for Filter Paper

In operation the upper portion of the apparatus is lifted off and a circle of the paper to be tested is laid across the 2-in. opening in the base. The upper half is then replaced, the wire screen supporting the filter paper and preventing the pressure underneath from bursting it. The stopcock regulating the supply is turned on slowly until the water overflows the cup A as well as the dam E. A 100-cc. volumetric flask is then placed underneath E and the number of seconds which are required for the flask to fill to the 100-cc. mark is determined by a stop watch. The penetrability figure is the number of seconds which are required for 100 cc. of distilled water at 20° C. to pass through a circle of the filter paper 2 in. in diam. under a constant 9-in. head. Obviously the penetrability figure varies inversely with the speed of the paper, *i. e.*, the slower the paper, the higher is the penetrability figure, and vice versa.

Effect of Temperature

Regaud-Monin has pointed out[4] that the temperature of the water has a marked bearing on the speed of filtration. It was found that water at 30° C. passes through a paper more than twice as rapidly as water at 0° C. under otherwise similar conditions. Table I is given in order to correct values obtained at a temperature other than 20° C.:

Table I

Temperature ° C.	Correction Factor
0	0.563
10	0.769
15	0.883
20	1.000
25	1.124
30	1.256

Effect of Long Filtration

It is well known that a filter paper will slow up considerably after having been used for a short time, even though the solution filtered does not contain sufficient precipitate to fill up the pores appreciably. This also holds true when distilled water alone is used, and is due to hydration and expansion of the fibers. During our investigation of the various factors affecting the penetrability of filter paper we have determined the effect of long filtration under a constant head. Some of the results are shown in Fig. 3.

In order to determine the relative effect of time upon speed of filtration an unusually slow paper and a fast paper were selected, and the penetrability of each sample was taken immediately and at the end of 10- or 20-min. periods for 1 hr. in the case of the slow paper, and for 2 hrs. in the case of the fast paper, allowing distilled water to run through the paper continuously during the intervals. In Fig. 3 A and A′ are the curves of two fast papers, taken from the same box, and B and B′ are the curves of two circles taken from a box of slow paper. The water was maintained at 20° C., and precautions were taken to keep it clean as well as all parts of the apparatus with which the water came in contact.

It will be seen that in the case of one of the fast papers, which originally had a penetrability of about 25 sec., the penetrability was slowed down to 1000 sec. by allowing distilled water to run through it for 2 hrs. Obviously, to obtain the greatest speed efficiency, the fastest paper that will hold the precipitate in question should be employed; the solution should be filtered as hot as possible, and the entire operation should be carried through without any unnecessary delay.

Penetrability Figures

The penetrability figures obtained upon several brands of well-known quantitative filter papers are given in Table II. The tests were made on five circles taken at random from each lot and the figure given is the average of the five tests.

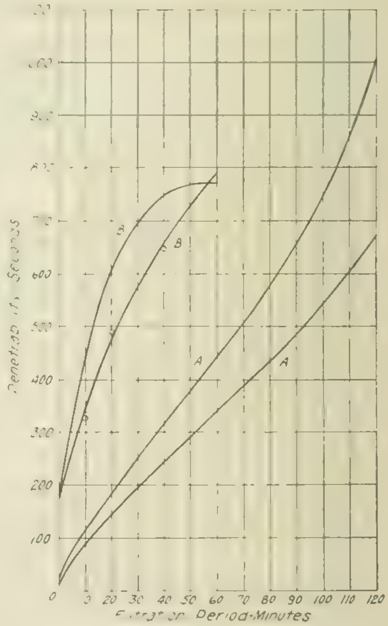

Fig. 3

A—Fast Paper (A. D. L.); B—Slow Paper (Whatman) No. 44

Table II

	Penetrability Seconds
Paper A (rapid, double washed, for general all-round use)	
Lot 1	16
Lot 2	20
Lot 3	20
Paper B (single washed, thin, rapid)	
Lot 1	16
Lot 2	16
Paper C (double washed, extra rapid, for gelatinous precipitates)	8
Paper D (double washed, very low ash)	
Lot 1	28
Lot 2	78
Lot 3	61
Paper E (dense formation, specially made for finest precipitates)	
Lot 1	85
Lot 2	54
Lot 3	120

It will be noted that paper C is about ten times as rapid as paper E.

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[4] *Papeterie*, **42** (1920), 818.

Quantitative Method for Determination of Peroxidase in Milk[1]

By Frank E. Rice[2] and Torataro Hanzawa[3]

Department of Chemistry, Cornell University, Ithaca, New York

A SATISFACTORY method for the quantitative determination of peroxidase in milk is described in this paper. It should find application in determining if milk has been heated to a temperature much above the usual pasteurizing temperature. If reconstituted powdered or evaporated milk or if boiled milk has been added to raw milk, application of this method will give proof of the fact, whereas qualitative tests for peroxidase will give no indication.

....

No method for making quantitative comparisons of peroxidase activity is found in the literature, although practically all other enzymes of milk are estimated quantitatively. Many qualitative tests for peroxidase have been suggested. In all of these, hydrogen peroxide is present, together with some reagent which undergoes a change in color when oxidized, such as guaiacol, paraphenylenediamine, benzidine, pyramidone, ortol, and other photographic developers. The peroxidase is believed to act as a carrier of oxygen from the hydrogen peroxide to the dye. Attempts to modify some of the qualitative tests so that quantitative interpretations could be made were not entirely successful. It was possible to compare the peroxidase activity of different samples only in a general way.

Bach and Chodat[4] have suggested a method for quantitatively determining peroxidase in extracts from plant tissue, involving the oxidation of soluble pyrogallol to insoluble purpurogallin. When an excess of hydrogen peroxide and pyrogallol is present, the extent to which the reaction takes place depends upon the amount of the peroxidase, all other conditions such as time and temperature being the same. The weight of the final product is taken as a measure of the peroxidase activity.

The reaction is probably as follows:

$$\underset{\text{pyrogallol}}{3C_6H_3(OH)_3} + 2O = \underset{\text{purpurogallin}^5}{C_6H_3(OH)(OOC_6H_3(OH)_2)_2} + 2H_2O$$

Application of Bach and Chodat Method to Milk Samples

Ten cc. of milk were diluted with 50 cc. of water, and treated with 20 cc. of 5 per cent pyrogallol and 10 cc. of 1 per cent hydrogen peroxide. The mixture was stirred well, allowed to stand several days at room temperature (19° to 21°), and filtered on a dried and weighed filter. The precipitate was first washed with a freshly prepared mixture similar in composition to the precipitating solution, made by adding to 50 cc. of distilled water 20 cc. of 5 per cent pyrogallol and 10 cc. of 1 per cent hydrogen peroxide. It was finally washed with 100 cc. of distilled water and dried to constant weight at the temperature of boiling water.

TIME NECESSARY FOR COMPLETING THE REACTION—Although Bach and Chodat found that 24 hrs. was sufficient time to complete the reaction with plant juice extracts, with milk much longer time is necessary before the reaction has reached an equilibrium. Seven days is a satisfactory reaction time.

Expt. 1—Several identical mixtures were started on the same sample of milk. Each day one was filtered and weighed. In all cases 10 cc. of milk were used, and the weights of purpurogallin in Table I are given in mg. per 10 cc. of milk.

Table I

Time of Reaction Days	Raw Skim Milk	Pasteurized Skim Milk	Boiled Skim Milk
1	14.6	10.4	.....
2	25.4	19.8	.....
3	28.0	21.4	0
4	30.5	26.8	.....
5	31.2	27.0	Trace
6	31.8	28.0	.....
7	31.5	28.2	8.2
8	32.0	29.0	.....

EFFECT OF PRESENCE OF AIR—In the sample containing boiled skim milk (Table I) it is seen that some purpurogallin precipitated out in 7 days. The precipitation took place at the surface of the liquid and since the determinations were run in beakers, it was believed that the air had influenced the reaction. Certainly there should be no peroxidase in boiled milk.

The following observations were made: A solution containing boiled milk together with pyrogallol alone, or with hydrogen peroxide, and in presence of air precipitated purpurogallin after about 5 days. A mixture of boiled milk, pyrogallol, and hydrogen peroxide, covered with paraffin or filled into a bottle so that air was excluded, never precipitated purpurogallin. From this it is evident that it is necessary to prevent the access of air to the reacting mixture; otherwise all the purpurogallin precipitated could not be attributed to the action of peroxidase.

To avoid this difficulty, glass-stoppered bottles of 100- to 130-cc. capacity were employed. After the measured amounts of milk, water, hydrogen peroxide, and pyrogallol had been mixed, the bottles were entirely filled with a solution of hydrogen peroxide and pyrogallol of composition similar to that which was already in the mixture, and tightly stoppered.

REMOVAL OF FAT FROM RESIDUE—Since any fat in the milk would probably remain on the filter, it was desirable to wash the precipitate with a fat solvent. Ethyl ether readily dissolves purpurogallin, but petroleum ether does not.

Expt. 2—Two of the purpurogallin residues from skim milk were washed five times with petroleum ether, and after each washing the filter was dried and weighed.

	Residue A Mg.	Residue B Mg.
Precipitate	36.0	31.8
After 1st washing	30.8	27.0
After 2nd washing	30.4	26.8
After 3rd washing	30.2	27.0
After 4th washing	30.4	27.0
After 5th washing	30.4	27.0

These results showed that in applying the method to milk it was necessary to wash the residue finally to remove the fat. In all subsequent determinations after the last washing with water the filters were dried and washed twice with petroleum ether before finally drying and weighing.

PROPORTIONS OF HYDROGEN PEROXIDE AND OF PYROGALLOL—In order that the enzyme may have opportunity to exert its full effect, it is important that hydrogen peroxide and pyrogallol be present in excess. In the two following experiments the effect of varying these constituents was determined:

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[1] Presented before the Division of Biological Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Assistant Professor of Agricultural Chemistry, Cornell University.

[3] Professor of Chemistry, Agricultural College of Japan.

[4] *Ber.*, **37** (1904), 1342.

[5] H. Wichelhaus, *Ibid.*, **5** (1872), 846.

Expt. 3—In each mixture the hydrogen peroxide was varied, while the other ingredients were kept constant.

1 Per cent Hydrogen Cc.	Hydrogen Peroxide Per cent	Water Added Cc.	5 Per cent Pyrogallol Cc.	Skim Milk Cc.	Purpurogallin in 7 Days Mg.
2	0.025	58	10	10	22.4
4	0.050	56	10	10	27.4
6	0.075	54	10	10	27.6
8	0.100	52	10	10	27.2
10	0.125	50	10	10	27.4
12	0.150	48	10	10	28.2
14	0.175	46	10	10	27.6
16	0.200	44	10	10	28.0
18	0.225	42	10	10	27.4
20	0.250	40	10	10	28.4

Expt. 4—The proportion of pyrogallol was next varied.

5 Per cent Pyrogallol Cc.	Pyrogallol in Mixture Per cent	Water Added Cc.	Hydrogen Peroxide Cc.	Skim Milk Cc.	Purpurogallin in 7 Days Mg.
2	0.125	58	10	10	18.8
4	0.250	56	10	10	22.6
6	0.375	54	10	10	28.4
8	0.500	52	10	10	31.2
10	0.625	50	10	10	31.0
12	0.750	48	10	10	31.6
14	0.875	46	10	10	31.4
16	1.000	44	10	10	31.6
18	1.125	42	10	10	30.8
20	1.250	40	10	10	31.4

These results show that all proportions of hydrogen peroxide above 0.05 per cent and of pyrogallol above 0.5 per cent are sufficient. In further experiments, therefore, 10 cc. of hydrogen peroxide were continued, but the quantity of pyrogallol was reduced to 10 cc.

COMPARISON OF WHOLE AND SKIM MILK—A sample of skim milk taken from a cream separator was compared with the whole milk from which it came. Ten cc. of the whole milk yielded 34.2 mg. of purpurogallin; with the skim milk there were obtained 32.0 mg. In another instance whole milk was placed in a tube, warmed slightly, and centrifuged. Ten cc. of the skim milk layer gave 31.8 mg., and an equal volume of the whole milk 33.2 mg. purpurogallin.

Exceedingly great difficulty was always found in filtering the mixture containing the whole milk, while the skim milk mixture filtered readily. For this reason it is recommended that before a sample of milk be run by the pyrogallol method it be first centrifuged to remove most of the fat.

Description of Method

Place sample in a tube, warm slightly, and centrifuge. Transfer 10 cc. of the skim milk to a glass-stoppered bottle of about 100-cc. capacity, add 50 cc. of distilled water, followed by 10 cc. of 5 per cent pyrogallol and 10 cc. of 1 per cent hydrogen peroxide. Shake well, and fill up the bottle with a solution prepared by mixing 60 cc. of water with 10 cc. of 1 per cent hydrogen peroxide and 10 cc. of 5 per cent pyrogallol. Stopper tightly, and let stand for 7 days[6] at room temperature. Filter on a weighed Gooch, wash the precipitate, first with the pyrogallol-hydrogen peroxide mixture just described, and finally with distilled water. Use no more than the necessary quantity of water in the washing, since purpurogallin is slightly soluble. When the washings do not give a dark blue color with ferric chloride solution, all the pyrogallol has been removed and the filter has been sufficiently washed. Dry the filter thoroughly, wash two or three times with petroleum ether, dry, and weigh. The weight of purpurogallin (in mg.) yielded by 10 cc. of milk is to be called the *peroxidase number*.

Relation between Amount of Peroxidase in Milk and the Peroxidase Number

In order to show that the relative amounts of peroxidase in milk could be determined by the amount of purpurogallin precipitated, raw and boiled skim milk were mixed in various proportions and run by regular method (Expt. 5):

Raw: Boiled	100:0	75:25	50:50	25:75	0:100
Peroxidase numbers	28.2	21.4	15.4	8.2	0
Ratio	100	75.8	54.6	29.0	0

Effect of Pasteurizing and of Preservatives on Peroxidase Activity

In Expt. 1 a comparison may be made of the peroxidase numbers of raw and pasteurized milk. The pasteurization was brought about by bringing the milk to 145° F. in 10 min., holding at that temperature for 30 min., and finally cooling to 60° F. in 10 min.

Expt. 6—In this experiment the peroxidase numbers of portions of skim milk were determined after different heat treatments. The samples were heated at the various temperatures for 30 min. except for the blank which was untreated; the peroxidase numbers were as follows: blank, 31.8; 145° F., 25.6; 155° F., 24.2; 165° F., 0; 180° F., 0.

Heating at 145° F. and at 155° F. is seen to reduce the peroxidase number to some extent, though the critical point is evidently between 155° and 165°.

A sample of skim milk, 10 cc. of which yielded a peroxidase number of 30.2 when fresh, gave 27.6 after being held at 40° F. for 2 days.

A portion of the same milk was preserved with 1 per cent mercuric chloride, and to another portion was added formaldehyde at the rate of 1 cc. to a pint. The sample containing mercuric chloride could not be determined on account of a precipitate, resulting probably from a precipitation of the casein by the mercury. The sample containing formaldehyde gave a peroxidase number of 0, which is probably due to the reducing effect of the formaldehyde.

Evidently neither mercuric chloride nor formalin can be used to preserve samples of milk in which the peroxidase number is later to be determined.

When milk is held on ice for 2 days the peroxidase activity is seen to fall off to some extent.

Summary

1—The method proposed by Bach and Chodat for the estimation of peroxidase in plant juices is adapted with modifications for milk.

2—The method depends upon the oxidation of pyrogallol by hydrogen peroxide, the reaction being catalyzed by peroxidase. The weight of purpurogallin which precipitates out (mg. resulting from the action of 10 cc. of milk) is called the "peroxidase number."

3—Seven days are necessary for the reaction to reach an equilibrium. Since in this length of time air is a factor in the precipitation of purpurogallin, the reaction must take place in absence of air.

4—To remove fat the residue is washed with petroleum ether, in which purpurogallin is insoluble.

5—Whole milk and skim milk are about equal in peroxidase activity.

6—By mixing raw and boiled milk in varying proportions it was shown that the peroxidase number varies quite regularly with the concentration of peroxidase.

7—Heating milk below 155° F. for 30 min. reduces but does not destroy peroxidase activity. Holding on ice for 2 days reduces the action slightly.

8—Samples of milk for peroxidase estimation cannot be preserved with mercuric chloride or formaldehyde.

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[6] Other modifications of the method of Bach and Chodat have been offered, such as that of Willstätter and Stoll [*Ann.*, **416** (1918), 21]. In general these methods have been adapted to the determination of peroxidase in fractions from plant materials. In these fractions the peroxidase activity is much greater than in milk, and for this reason a considerable amount of purpurogallin is produced in a very short time. Under such conditions the reaction is not allowed to run to completion but is stopped after a short period and the amount of purpurogallin produced during this time is taken as a measure of the amount of peroxidase. In milk, however, the activity of the enzyme is so weak that even by allowing the reaction to go to completion (which requires about 7 days), a relatively small weight of purpurogallin is obtained. On this account the authors consider it wise to allow the full time for the determination; however, it would be possible to obtain comparative results in from 1 to 3 days.

The Preservation of Fish Frozen in Chilled Brine[1,2]

II—The Keeping Quality of the Fish

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The following paper concludes the work published last year on "The Preservation of Fish Frozen in Chilled Brine." In this part of the work, fish were frozen in air at −10° and in 15 per cent brine at its freezing point. In general, fish frozen in air lost somewhat in weight, while there was a slight gain upon freezing in brine. On storage, brine-frozen fish usually lost less than air-frozen fish. Brine-frozen fish could be successfully glazed, after a preliminary rinsing in cold water. The method of freezing had no effect on the amounts of fat-free solids, ammonia, and amine nitrogen, on the rate of decomposition after removal from freezer storage, or on the number or general character of the bacterial flora in the skin, flesh, and intestines. Cooking tests showed that air-frozen and brine-frozen fish were perfectly edible at the end of the storage periods, but the texture and flavor of the latter were slightly superior to the other.

During the one or two hours that fish are in contact with cold brine during freezing by the newly advocated process of brine freezing, a small amount of salt is absorbed in spite of attempts to prevent it.[1,*] The extent of penetration varies in different species of fish, and appears to be influenced somewhat by the presence of fat in the tissues, the fatty tissues not absorbing as much as the lean.

The texture of brine-frozen fish differs from that of air-frozen fish in that during chilling and freezing the muscular tissue of the former is little affected, whereas that of the latter is somewhat altered as a result of the separation of water from the tissues.[2] Because of this difference in texture and also of the fact that the brine-frozen fish have a small amount of salt in the outer layers, the keeping qualities of the two kinds of fish during storage may show interesting differences.

Plank and Ehrenbaum[3] found that during 30 hrs.' freezing in air at −7° C. and 85 per cent relative humidity cod lost 3 to 4 per cent, haddock about 5 per cent, and flat fish like flounders about 6 per cent, and that during freezing in brine there was no loss and quite often a slight gain in weight. During storage the fish in the majority of instances lost in weight, and among fish of the same species but of different size the loss was approximately in inverse proportion to the cube roots of the weights. These authors show that the evaporation of water is lower in fatty fish and is less the more nearly the form of the fish resembles a sphere, in which shape the proportion of surface to mass is least. A few examples of weight changes observed by them are given in Table I. They show that the weight losses in fish hanging free in a room at −7° C. are very large. Protected by wrapping in parchment paper, the fish changed in weight but little. Droogleever Fortuyn[4] reports a loss in weight of 12 to 24 per cent in soles stored for 4 to 5 wks. at −2° to −6° C.

METHOD OF INVESTIGATION

Uneviscerated weakfish (*Cynoscion regalis*), whiting (*Merluccius bilinearis*), mossbunkers (*Brevoortia tyrannus*), butterfish (*Poronotus triacanthus*), and spot (*Leiostomus xanthurus*) were frozen in air and in brine in the manner previously described.[1] The brine solution was approximately 15 per cent and was held at its freezing point during the freezing of the product. All brine-frozen fish were frozen singly.

TABLE I—EXAMPLES OF WEIGHT CHANGES IN STORED FISH OBSERVED BY PLANK AND EHRENBAUM

Fish	Manner of Freezing	Manner of Storing at −7° C. and 85% Relative Humidity	Duration of Storage Period Days	Change in Weight before Thawing Per cent	Change in Weight after Thawing in Air Per cent
Mackerel	In air at −7° C.	Uneviscerated, hanging free, glazed	66	−12.5	.....
Mackerel	In concentrated NaCl at −14° C.	Uneviscerated, hanging free, glazed	84	−17.2	.....
Mackerel	In NaCl brine by Ottesen method at −15° C.	Uneviscerated, wrapped in parchment paper	50	.....	−0.3
Plaice	In air at −12° C.	Uneviscerated, hanging free, glazed	40	−23.5	.....
Plaice	In air at −12° C.	Uneviscerated, hanging free, glazed	56	−36.6	−33.3
Plaice	In NaCl brine by Ottesen method at −15° C.	Eviscerated, wrapped in parchment paper	50	.....	+ 0.5
Flounders	In air at −7° C.	Uneviscerated, in open basket	165	−60.3	.....

Most of the air-frozen fish were frozen in pans and stored in the form of solid cakes of fish; a few were frozen singly in order to facilitate the determination of individual weight changes.

After glazing, the weakfish, mossbunkers, and spot were stored for 5 mo. and part of the whiting for 3 mo. in a room whose temperature during these periods remained fairly constant at −10° F.; during the next 3 mo. of storage, beginning March 1, the temperatures fluctuated between −5° and +15° F. The remainder of the whiting were stored for 6 mo. at a uniform temperature of 12° to 15° F. in a room in a separate storage house. The fish were packed in covered wooden boxes lined with vegetable parchment paper.

PHYSICAL TESTS

Whiting frozen singly in air at −10° F. lost 2.32 per cent of their weight in the 18.5 hrs. following their entrance into the freezer. The same species of fish gained 0.15 per cent in weight during 1 hr.'s freezing in brine, and during the succeeding 17 hrs. in cold storage at −10° F. gained 0.38 per cent more in weight. Surface water was removed from these fish before freezing in air. The apparent loss in weight of fish during the freezing is higher if this water is not taken into account. For example, it was found that whiting, after washing in water, when frozen singly, lost in 3, 6, and 22 hrs. 2.54, 3.60, and 4.03 per cent in weight, respectively, when the wash water was allowed to remain on the surface, and 1.55, 2.44, and 2.74 per cent, respectively, when the exterior of the fish was freed from excess moisture prior to the initial weighing and entrance into the freezer. When whiting, the exterior of which had been dried, were frozen in a pan in a compact layer, the loss in 3, 6, and 22 hrs. was much smaller and more uniform, being 0.33, 0.59, and 0.80 per cent, respectively.

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[1] Received October 31, 1921.

[2] Published by permission of the Secretary of Agriculture.

[3] Food Research Chemist, Bureau of Chemistry.

[*] Numbers in text refer to Bibliography at end of paper.

Table II—Percentage of Fat-Free Solids in Flesh of Brine-Frozen and Air-Frozen Fish during Storage[1]

B. = Brine-frozen; A. = Air-frozen

Date of Analysis	Weakfish		Mossbunkers		Spot		Whiting			
							No. 1		No. 2	
	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.
October 11, 1919	19.43	20.05	22.47	19.11	21.54	19.05	...	...	...	...
December 3, 1919	...	...	...	...	...	...	17.66	17.17	17.66	17.17
March 8, 1920	20.20	20.18	20.20	18.23	21.82	19.78	18.86	18.16	16.67	18.67
June 9, 1920	19.13	...	21.64	20.32	20.27	19.81	18.57	18.51	18.66	18.45

[1] The weakfish, mossbunkers, and spot were stored at −10° F. from October 6, 1919, to March 1, 1920, and at −5° to +15° F. from March 1 to June 1920. Whiting No. 1 was stored at 12° to 15° F. beginning December 3, 1919. Whiting No. 2 was stored at −10° F. from December 3, 1919, to March 1920, and at −5° to +15° F. from March 1 to June 1920.

Table III—Percentage of Ammonia and Amine Nitrogen in Flesh of Brine-Frozen and Air-Frozen Fish during Storage[1]

B. = Brine-frozen; A. = Air-frozen (Dry Basis)

Date of Analysis	Weakfish		Mossbunkers		Spot		Whiting			
							No. 1		No. 2	
	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.
October 11, 1919	0.091	0.094	0.092	0.100	0.091	0.108	...	...	...	...
December 3, 1919	...	...	...	...	...	...	0.087	0.093	0.087	0.093
March 8, 1920	0.082	0.086	0.084	0.093	0.079	0.091	0.121	0.127	0.104	0.099
June 9, 1920	0.094	0.086	0.101	0.096	0.101	0.099	0.134	0.122	0.098	0.095

[1] See footnote to Table II.

Table IV—Percentage of Ammonia and Amine Nitrogen in Flesh of Brine-Frozen and Air-Frozen Fish during 8 Days' Holding at 50° to 55° F. after Storage for 3 to 5 Mo. at Freezer Temperatures (Dry Basis)

B. = Brine-frozen; A. = Air-frozen

Number of Days Held at 50°–55° F.	Weakfish after 151 Days' Storage at −10° F.		Mossbunkers after 144 Days' Storage at −10° F.		Spot after 144 Days' Storage at −10° F.		Whiting			
							No. 1 after 96 Days' Storage at 12–15° F.		No. 2 after 96 Days' Storage at −10° F.	
	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.
0	0.082	0.086	0.084	0.093	0.079	0.091	0.121	0.127	0.104	0.099
1	0.082	0.098	0.091	0.097	0.100	0.103	0.144	0.131	0.114	0.115
2	0.095	0.095	0.099	0.098	0.097	0.096	0.152	0.165	0.122	0.134
5	0.129	0.115	0.135	0.118	0.118	0.114	0.165	0.172	0.178	0.138
8	0.170	...	0.154	0.144	0.149	0.169	0.205	0.210	0.216	0.189

WEIGHT CHANGES UPON STORAGE—That the change in weight of frozen fish during storage need not be so great as reported by European investigators is indicated by the results which were obtained in the following study of weight changes in weakfish and whiting stored at the comparatively low temperatures prevalent in cold storage houses in this country. For these experiments the fish, after freezing singly in air and in brine, were weighed individually, then glazed, and reweighed at the end of the periods of storage, the glaze being removed before each weighing. Air-frozen weakfish lost 0.25 per cent during the first 5 mo. when the temperature was −10° F., the total loss during the entire 8 mo. of storage being 2.18 per cent. Air-frozen whiting lost 0.24 per cent during 3 mo. at −10° F., the total for the 6 mo. being 5.03 per cent. Brine-frozen weakfish and whiting gained 0.5 and 1.45 per cent, respectively, up to March 1, but suffered a loss during the remainder of the storage period when the temperature was higher and fluctuating, the amount being 2.90 and 2.12 per cent, respectively. The whiting stored at the comparatively high but uniform temperature of 12° to 15° F. lost considerably more in weight, the air-frozen and brine-frozen fish losing 9.55 and 6.48 per cent, respectively, during the entire 6 mo. It should be remarked that the latter storage temperature is higher than that which is generally employed in the storage of fish in this country.

The increase in the weight of the brine-frozen fish in the early storage period was rather surprising. It may possibly be that a small amount of moisture is attracted to and held by the salt in the exterior tissues of these fish.

GLAZING—The most convenient and efficient method of preserving the exterior appearance of fish and of minimizing the evaporation of water during storage is by means of an ice glaze. Just after the fish have frozen through completely they are dipped momentarily in cold water, a thin film of ice forming on the surface. The treatment is repeated until a substantial glaze is provided. The original glaze may remain for 4 or 5 mo. or even longer on fish which are packed in boxes and stored at low uniform temperatures. Where the fish are stacked in bins in the storage room without boxing, reglazing at intervals of 3 mo. or less may be necessary.

When brine-frozen fish are immersed in cold water immediately after removal from the brine, they do not take a glaze. It was thought at first that this would be a serious objection to the use of this method of freezing fish for storage. However, further attempts in this direction were successful. Fish which had been rinsed in cold water and then held in the storage room for 12 hrs. took a glaze as readily as the air-frozen fish.

Brine-frozen and air-frozen weakfish, whiting, mossbunkers, and spot were glazed and examined at the end of 5, 6, and 8 mo. storage. The fish were not reglazed during these periods. It was found that the brine-frozen fish retained the glaze fully as well as the air-frozen. The weakfish, mossbunkers, and spot, both air-frozen and brine-frozen, possessed a good glaze at the end of 5 mo. storage, although none of the fish had a glaze 3 mo. later, largely on account of the temperature fluctuations during the latter period of storage. The whiting retained a thin glaze at the end of 6 mo. The surface of the brine-frozen fish had a fresher and more attractive appearance than that of the air-frozen at the end of the maximum holding period.

Chemical Tests

SALT CONTENT—Analyses of the salt content of the two succeeding layers of muscular tissue $^3/_{32}$ in. thick just beneath the skin of whiting immediately after freezing in brine and after storage for 6 mo. seem to indicate that some of the penetrated salt travels inward during storage. The proportion of salt in the outer layer to that in the inner layer was about 2 : 1 at the beginning of storage, but the amounts present in the two layers after storage were usually less and were more nearly equal. Possibly there exists a tendency for the salt to distribute itself more or less uniformly through the tissues, although a definite conclusion on this point must await a more extended investigation. Such a decrease in the salt content of the outer layers might explain the lack of interference of the salt with the permanence of the glaze during storage.

TABLE V—NUMBER OF BACTERIA IN FISH AS AFFECTED BY FREEZING AND STORAGE

B. = Brine-frozen fish; A. = Air-frozen fish

EXPT. No.	FISH	Part of Fish	Number of Bacteria per Gram									Temperature of Storage[1] ° F.
			Before Freezing	Immediately after Freezing		After Storage for X Days		After Storage for Y Days		X Days	Y Days	
				B.	A.	B.	A.	B.	A.			
6037 (*b*)	Spot	Skin	....	6,900	9,000	....	....	....	....	...	...	...
		Flesh	....	4,100	260	....	....	....	....			
		Intestines	....	11,100	40,000	....	....	....	....			
6035 (*a*)	Spot	Skin	....	....	....	8,700	80,000	8,300	29,000	144	236	−10 to +15
		Flesh	....	....	....	700	640	390	430			
		Intestines	....	....	....	1,700	1,250	900	1,400			
6038	Butterfish	Skin	8,770	1,680	25,710	....	....	....	....	...	...	...
		Flesh	2,210	420	2,170	....	....	....	....			
		Intestines	530	500	0	....	....	....	....			
6034	Weakfish	Skin	....	....	....	30,900	8,800	23,000	12,900	151	243	−10 to +15
		Flesh	....	....	....	930	190	100	110			
		Intestines	....	....	....	4,000	10,200	1,200	9,400			
6035 (*b*)	Mossbunkers	Skin	....	....	....	8,200	27,000	7,000	17,400	144	236	−10 to +15
		Flesh	....	....	....	900	280	250	1,330			
		Intestines	....	....	....	8,000	6,900	1,600	6,000			
6042	Whiting	Skin	7,540	1,340	175	1,800	220	....	....	108	...	−10
		Flesh	1,600	0	0	100	40	....	....			
		Intestines	193,280	350	2,130	4,600	3,200	....	....			
6043	Whiting	Skin	200	3,500	240	26,000	6,000	3,200	350	96	188	−10 to +15
		Flesh	910	0	0	8,300	120	100	50			
		Intestines	3,000	420	0	16,000	2,600	900	460			
	Whiting	Skin	....	....	....	380	90	600	228	96	188	12 to 15
		Flesh	....	....	....	40	0	350	16			
		Intestines	....	....	....	51,100	4,800	9,200	2,600			

[1] The temperature for X days was fairly constant at −10° F. The remainder of the time the temperature fluctuated between −5° and +15° F.

FAT-FREE SOLIDS—The percentage of fat-free solids of fresh fish does not vary appreciably in individuals of the same species and size. Determinations of fat-free solids in stored fish afford a means of estimating the extent of the drying out, the proportion of this constituent increasing with the desiccation of the product. As shown in Table II, there is a tendency toward decreased moisture content in the older storage samples. However, there are no pronounced differences attributable to the method of freezing, as was apparent from the results of gross weight determinations on individual fish.

AMMONIA AND AMINE NITROGEN—As a chemical method for following the changes in the flesh of fish during storage, determinations of the ammonia and amine content by a modified Folin aeration method[5] were employed. It had previously been found that the amounts of these bases increased slowly in the flesh of frozen fish during storage.[6] Their accumulation in the flesh is the result of the action of tissue enzymes, of bacteria, or of both. The content of the bases, therefore, is an index of quality only in the sense that it indicates somewhat the extent of the aging which has taken place. Supported by careful physical and bacteriological examinations it is of assistance in the determination of wholesomeness. During storage the content of ammonia and amine nitrogen increased in all fish except the weakfish, mossbunkers, and spot which had been frozen in air. (Table III.) Except in the case of Whiting 1, however, the increases were exceedingly small. At the end of the storage period in June, the percentages of these bases were slightly higher in the brine-frozen fish than in the air-frozen, though the difference is not sufficiently great to justify the conclusion that a difference in keeping quality is indicated.

RATE OF DECOMPOSITION—Additional chemical evidence of the relative keeping qualities of air- and brine-frozen fish was obtained by comparing the rate of decomposition of the fish after removal from storage. The fish, before thawing, were placed in a compartment of a large household refrigerator where the temperature was 50° to 55° F., and were examined immediately and at the end of 1, 2, 5, and 8 days for the content of ammonia and amine nitrogen in the flesh. The experiments (Table IV) did not indicate any consistent difference in the keeping qualities resulting from the method of freezing.

Several whiting which had been stored for 6 mo. were cooked (fried) and tasted by several persons. The consensus of opinion was that the brine-frozen fish had a slightly better flavor than the air-frozen, though both kinds were perfectly edible. A difference in texture of the cooked product was also noted. The flesh of the brine-frozen product seemed a trifle firmer. On comparing sections of the muscular tissue prior to cooking it was observed that it was possible to squeeze more of the juices from the samples of air-frozen fish than from those of the brine-frozen. Apparently the difference in texture produced during the chilling and freezing persists during the storage period.

BACTERIOLOGICAL TESTS*

The surface of fresh caught fish† contains many bacteria obtained from the water, air, hold of the boat, and other sources. Quite frequently also the flesh harbors bacteria which may have entered the tissue through the skin, the wall of the belly cavity, or through the blood system by way of the gills. Many investigators have found *B. coli* in the intestines of fish taken from polluted water.[7] In general, the digestive tract contains bacteria when food is present, but is usually sterile when food is absent. Important contributions on this subject have been made by Hunter,[8] Obst,[9] Browne,[10,11] and others.

When fish are immersed in chilled brine the bacteria on the surface may be affected in two ways. The number may be increased or decreased, depending on the purity of the brine from a bacterial standpoint. Furthermore, the entrance of small amounts of brine into the superficial tissues may carry some of the surface bacteria through the skin into the flesh. Obviously the prevention of the former condition is accomplished by keeping the brine as free from bacteria as possible. The latter may be minimized by preliminary cleansing of the surface of the fish and by the adoption of procedures, such as precooling of the fish in air, which will tend to reduce the extent of salt penetration during the freezing.

Whiting, weakfish, butterfish, spot, and mossbunkers were examined for bacteria at various stages in the processes of freezing in brine and in air and at the end of periods of storage. The slime and scales were aseptically removed from an area near the dorsal fin and the exposed skin was removed with sterile instruments, after which a portion of the underlying flesh was cut out. Likewise the contents of a section of the intestines were aseptically removed. The three samples were macerated by shaking in flasks with bits of sterile broken glass in sterile water, and aliquot portions plated on plain agar. The plates were incubated at 20° C.

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* The bacteriological examinations were made by Mr. C. H. Werkman, Assistant in Poultry and Egg Handling, Food Research Laboratory, Bureau of Chemistry, and Drs. Albert C. Hunter and Stuart A. Koser, Bacteriologists, Microbiological Laboratory, Bureau of Chemistry.

† The term "fresh caught" is here applied to the fish as landed from the fishermen's boats.

The figures in Table V give the average of three tests of composite samples of two fish each. The variation in the extent of bacterial contamination among the individuals of the different species before freezing is quite great and renders difficult an interpretation of the results of this nature. The data show, however, that there are no consistent differences in the numbers of bacteria in the skin, flesh, and intestines of the various fish before and after freezing and after storage, which might be attributed to the method of freezing.

Examination of the character of the bacterial flora in the fish failed to reveal outstanding differences in the two sets of fish. The predominating microörganisms before and after storage appeared to be mainly those which are usually present in air and water. Among the bacteria identified were *M. citreus* Sternberg, *M. luteus* Cohn, *M. aureus*, *M. flavus*, *M. roseus*, *M. aquatilis*, *staphylococcus aureus*, *albus* and *citreus*, *Bact. refractans* Wright, and *Bact. desidiosum* Wright. Pigment-producing yeasts and various molds, particularly *Aspergillus niger*, were fairly common.

It thus appears that there is very little choice between the two methods from the standpoint of bacterial decomposition during storage.

Bibliography

1—L. H. Almy and E. Field, "The Preservation of Fish Frozen in Chilled Brine. I—The Penetration of Salt," This Journal, **13** (1921), 927.

2—R. Plank, E. Ehrenbaum and K. Reuter, "Die Konservierung von Fischen durch das Gefrierverfahren," *Abhandlungen zur Volksernahrung*, issued by the Zentral-Einkaufsgesellschaft, **5** (1916), 218.

3—R. Plank, E. Ehrenbaum and K. Reuter, *Loc. cit.*, 97, and facing 180 and 196.

4—J. M. Bottemaine, "Notes on the Investigation of Preserving Fish by Artificial Cold," Preliminary Report, 3rd International Congress of Refrigeration, 3rd Section (The Netherlands), Washington-Chicago, **1913**, 25, 26.

5—E. D. Clark and L. H. Almy, "A Chemical Study of Food Fish. The Analysis of Twenty Common Food Fishes with Especial Reference to the Seasonal Variation in Composition," *J. Biol. Chem.*, **33** (1918), 486.

6—E. D. Clark and L. H. Almy, "A Chemical Study of Frozen Fish in Storage for Short and Long Periods," This Journal, **12** (1920), 656.

7—S. C. Prescott and C.-E. A. Winslow, "Elements of Water Bacteriology," 3rd Ed., John Wiley & Sons, Inc., **1915**, 141.

8—A. C. Hunter, "Bacterial Decomposition of Salmon," *J. Bact.*, **5** (1920), 353.

9—M. M. Obst, "A Bacteriologic Study of Sardines," *J. Infect. Dis.*, **24** (1919), 158.

10—W. W. Browne, "The Presence of *B. Coli* and *B. Welchii* Groups in the Intestinal Tract of Fish (*Stenomus chrysops*)," *J. Bact.*, **2** (1917), 417.

11—W. W. Browne, "Do Bacteria Play an Important Part in the Initial Stages of Decomposition of Fish during Storage in Ice?" *Abstracts Bact.*, **2** (1918), 6.

Report on Chemo-Medical Research

Under the title of "The Future Independence and Progress of American Medicine in the Age of Chemistry," the Chemical Foundation is circulating the report of the Committee on Chemo-Medical Research, appointed by the American Chemical Society in January 1919.

The report draws a lesson from the results accomplished during the war, when chemists, pharmacologists, and experimental pathologists joined in defensive and offensive work on poison gas at the American University Experiment Station. Great results may be expected in the battle against disease, says the report, through *coöperation under ideal conditions of time and equipment for research.*

How can chemistry, coöperating now with medicine as it coöperated with the war and naval departments, help best in the battle against disease? The constructive chemist can serve in three ways. First, he can aid by the preparation of specific medicaments for the cure or alleviation of specific diseases, either by the synthesis of new products or by the improvement of natural remedies already known. So, too, the study of the pure principles of our organs of secretion opens up a field rich in promise; and another great line of effort in this direction should be the attempt to isolate the pure principles of antitoxins and serums. The third opening for the constructive chemist is the complete ultimate analysis of the constituents of our body cells and the components of our blood and tissues, together with the complete ultimate analysis of the components of our foods. For example, Fischer's work on the structure and chemistry of the sugars opened the way for all the more recent work on carbohydrate metabolism and its pathologic variations. His work on the amino acids forms the foundation of all modern work on protein metabolism. The physical chemist has an important part to play in this coöperation, for the matter of health is closely bound up in the delicate adjustment of speed of the various chemical reactions taking place in the body. Many of our bodily functions are dependent on the action of enzymes (or catalysts). So, too, in nerve and cell, the questions to be dealt with are largely those of colloidal chemistry.

While there are in the United States a number of institutes and foundations for medical research, there is none in which problems are approached primarily from the chemical standpoint. To a large extent, chemo-medical research in this country has followed a few lines opened up in Europe. The professor in the medical school has little time for concentrated work on fundamental problems. Almost the only research work of the government laboratories bearing upon health is that of the Public Health Service, and especially of the Hygienic Laboratory. Data in regard to the amount of medical research in industrial establishments have been hard to obtain. It may be said, however, although many pharmaceutical and chemical manufacturers maintain research organizations which have been an important factor in reaching our present stage of progress, no commercial establishment can maintain a staff of specialists in the various branches of science such as would be required to accomplish effective work of the character now required.

It must be said, without fear of contradiction, (the report concludes) that there is not a single organization whose purpose is a determined coöperative attack on the problems of disease and health, where intense chemical and physical research goes hand in hand with the medical and biological study of disease. The importance of chemistry and physics has been recognized, but the direction of research is still essentially in the hands of medical men. No one of the scientific groups alone should be entrusted with leadership. All are needed for coping successfully with the complex and formidable problems. Complete coöperation of a staff of experts, peers in every sense, each in his own field, with emphasis on the fundamental chemical and physical character of the problems, has nowhere been accomplished. Consequently it is proposed that the attack be actually coöperative, from the selection of the problem and the formulation of the plan of work through the whole concentrated effort to grapple with Nature and ultimately to conquer outpost after outpost of the complex world of life.

Petroleum Statistics

Production of petroleum in the United States in 1921 amounted to 469,639,000 bbls., representing an estimated value at the wells of $753,300,000. This is the greatest quantity ever produced in the United States in any one year and represents an increase of 26,237,000 bbls. over the production of 1920 and is more than double the quantity produced in the United States in 1912. World's production figures for 1921 are not yet known, but preliminary estimates indicate a total not far from 750,000,000 bbls., as compared with 695,000,000 bbls. produced in 1920.

Imports of crude oil into the United States during 1921 amounted to 125,307,000 bbls., as compared with 106,175,000 bbls. in 1920 and with 52,822,000 bbls. in 1919, these figures corresponding, respectively, to 27, 24, and 14 per cent of the domestic production of the past three years. Exports of crude oil during 1921 amounted to 8,940,000 bbls. and during 1920 to 8,757,000 bbls.

Estimated consumption (deliveries to consumers) of domestic and imported crude oil during 1921 amounted to 525,407,000 bbls., as contrasted with 530,474,000 bbls. in 1920. Consumption for the year just ended therefore amounted to 55,768,000 bbls. more than the country produced.

Errors Caused by Nitrates and Nitrites in the Determination of Arsenic by the Distillation Method, and a Means for Their Prevention[1]

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It has been found that nitrates and nitrites interfere in the official method of the Association of Official Agricultural Chemists for total arsenic in insecticides, causing low results. This is probably brought about by the formation of nitrosyl chloride, which passes into the distillate, and there slowly oxidizes the trivalent arsenic to the pentavalent form.

This interference can be prevented by the application of the method of Jannasch and Seidel in which hydrazine sulfate and sodium bromide are used as reducing agents. In addition to giving greater accuracy, this method hastens the volatilization of the arsenic, thereby decreasing the time and the amount of hydrochloric acid required.

THE determination of arsenic by the method of reduction and distillation as arsenic trichloride has been the subject of numerous investigations. An exhaustive review of the literature concerning this problem is given by Roark and McDonnell in a paper[2] describing the application of this method to the determination of arsenic in insecticides. After testing many substances, these authors selected cuprous chloride as the most suitable reducing agent. Following their work, the Association of Official Agricultural Chemists adopted this as an "official" method,[3] and it has since been used in the Bureau of Chemistry with generally satisfactory results. However, in the analysis of commercial calcium and lead arsenates it was found that sometimes duplicate determinations did not agree, and that the results were low in comparison with those obtained by the modified Gooch and Browning method.[4]

It was also observed that delay between distillation and titration accentuated the difference. Impurities in the reagents were at first suspected as the cause of the trouble, but after investigation it was proved that the disturbing factor lay in the sample itself.

The decrease in the titrations with the lapse of time indicated oxidation in the distillate and led the writers to suspect the presence of an oxidizing substance in the sample. In order to cause the effect noticed, the interfering substance or substances must either be volatile or produce volatile products which are oxidizers. These conditions, considered in connection with the process of manufacture of calcium and lead arsenates, practically limit the possible oxidizing substances to nitrates and nitrites. Qualitative tests on a sample of calcium arsenate giving discrepant results showed the presence of a considerable amount of nitrate and a trace of nitrite. Subsequent determination of the nitrogen in this sample gave results equivalent to 3.50 per cent of nitrogen pentoxide. In all cases in which trouble was experienced nitrates were found. Working upon this suggestion, experiments were planned to determine more definitely the action of nitrates and nitrites and to devise a modification of the method to overcome this source of error.

STANDARD SOLUTIONS

The following standard solutions were prepared:

ARSENIC ACID—A solution was prepared from solid arsenic acid which had been purified by several crystallizations from water. It contained 26.05 g. of arsenic pentoxide per liter, as determined by analysis both by the official distillation method[3] and by the Gooch and Browning method of reduction with potassium iodide and subsequent titration with standard iodine solution.

NITRATE SOLUTIONS—(1) a solution containing 10.0 g. of lead nitrate per liter; (2) a solution containing 4.954 g. of calcium nitrate per liter.

NITRITE SOLUTION—A solution containing 4.167 g. of sodium nitrite per liter (the same concentration of nitrogen as in the standard nitrate solutions).

EXPERIMENTAL PROCEDURE

The analyses were made on 25-cc. samples of the arsenic pentoxide solution to which were added varying amounts of the nitrate or nitrite solutions. (The weight of calcium arsenate usually taken for analysis is 1.5 g., so that on this basis the amount of nitrate introduced with 25 cc. of the standard nitrate solutions is equivalent to about 5.4 per cent of nitrogen pentoxide in a commercial sample.) In the experimental procedure the official method was followed except as noted, and all determinations were made in duplicate. The reducing agents were first introduced into the distillation flasks, then aliquot portions of the arsenic pentoxide and of the nitrate or nitrite solutions were added by means of pipets, followed by 100 cc. of concentrated hydrochloric acid. A total of 250 cc. of hydrochloric acid was used in each determination. The distillates were made to 1 liter, and aliquot parts were titrated according to the bromate method of Gyory,[5,6] as presented to the Association of Official Agricultural Chemists by the referee on insecticides and fungicides at the 1920 meeting. As the proceedings of this meeting have not yet been published, the details of the method will be quoted here:

> Transfer 200-cc. aliquots of the distillate to 500-cc. Erlenmeyer flasks, heat to 90° C., and titrate with the standard potassium bromate solution (1.688 g. potassium bromate to 1 liter of water standardized against arsenious oxide in approximately 2 *N* HCl), using methyl orange as indicator. The indicator should not be added until near the end of the titration, and the solution should be rotated continuously to avoid any local excess of the titrating solution. The end of the reaction is indicated by a change from red to colorless and is very sharp.

The first experiments showed conclusively that both nitrates and nitrites had a marked effect on the results. When 0.25 g. of lead nitrate was used the distillate in the receiving flask was decidedly yellow and even 0.05 g. caused a slight yellow coloration. Nitrites produced the same effect. This color disappeared when the distillates were made to volume in a liter flask. On heating, the distillate slowly destroyed the color of methyl orange, but the fading was not sufficiently rapid to interfere with the titration. Aliquot portions titrated at successive intervals showed a steady decline in the arsenic value.

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[1] Received October 22, 1921.

[2] THIS JOURNAL, 8 (1916), 327.

[3] Assoc. Official Agr. Chemists' Methods, 2nd edition (1920), 54.

[4] Dept. of Agriculture, *Chem. Bull.* 105 (1907), 166.

[5] *Z. anal. Chem.*, 32 (1893), 415.

[6] Enough experiments were made to show that the bromate method gave the same results as the iodine titration method, and it was used because of its directness and greater speed.

Table I—Effect of Nitrates and Nitrites on Determination of Arsenic by Distillation
(Arsenic pentoxide taken in each experiment 0.1303 g.)

Reducing Agents					Arsenic Pentoxide Found, Grams						Properties of Distillate	
Cuprous Chloride Grams	Additional Grams	Lead Nitrate Taken Grams	Calcium Nitrate Taken Grams	Sodium Nitrite Taken Grams	Titrated Immediately	Titrated after 4 Hrs.	Titrated after 1 Day	Titrated after 2 Days	Titrated after 3 Days	Titrated after (*) Days	Color	Bleaching Action on Methyl Orange at 90° C.
5	......	..	...	...	0.1303	....	....	0.1303	....	0.1303 (18)	None	None
5	......	0.05	...	...	0.1303	....	0.1279	0.1268	....	0.1258 (10)	Light yellow	Marked
5	......	0.25	...	...	0.1289	....	0.1146	0.1082	....	0.1051 (10)	Decided yellow	Marked
5	......	..	0.124	...	0.1301	0.1270	0.1200	0.1169	....	.....	Decided yellow	Marked
5	......	..	...	0.104	0.1257	....	0.1075	....	0.0950	0.0920 (5)	Decided yellow	Marked
15	......	0.25	...	...	0.1296	....	0.1220	0.1206	....	0.1186 (18)	Decided yellow	Marked
5	$FeSO_4$ 10	0.25	...	...	0.1276	....	0.1234	0.1215	....	0.1193 (18)	Decided yellow	Marked
5	$FeSO_4$ 10	..	0.124	...	0.1303	0.1291	0.1256	0.1235	....	.....	Decided yellow	Marked
5	NaBr 1	0.25	...	...	0.1277	....	0.1170	0.1120	....	0.1054 (18)	Decided yellow	Marked
5	NaBr 1	..	0.124	...	0.1303	0.1277	0.1195	0.1169	....	.....	Decided yellow	Marked
5	Aniline oil 1 (cc.)	0.25	...	...	0.1300	....	0.1262	....	....	.....	Decided yellow	Marked†
5	Aniline oil 5 (cc.)	0.25	...	..	0.1323	....	0.1297	....	....	.....	Decided yellow	Marked†
5	Aniline oil 5 (cc.)	..	...	0.104	0.1341	....	0.1329	....	....	.....	Decided yellow	Slight†
5	NH_4Cl 2	0.25	...	...	0.1292	....	....	0.1113	....	0.1043 (5)	Decided yellow	Marked
5	NH_4Cl 2+NaBr 1	0.25	...	...	0.1291	....	....	0.1103	....	0.1015 (5)	Decided yellow	Marked
5	Hydrazine sulfate 2	0.25	...	...	0.1303	....	0.1303	0.1303	....	0.1303 (18)	Light brown	None
5	Hydrazine sulfate 2	..	...	0.104	0.1303	....	0.1303	....	0.1303	0.1303 (5)	None	None
5	Hydrazine sulfate 2	..	0.124	...	0.1303	0.1303	0.1303	0.1303	....	.....	None	None
5	Hydrazine sulfate 1	0.25	...	...	0.1303	....	0.1300	....	0.1295	0.1291 (5)	None	Slight
5	Hydrazine sulfate 1	..	0.124	...	0.1303	0.1301	0.1298	0.1298	....	.....	None	Slight
5	Hydrazine sulfate 0.5+NaBr 1	0.25	...	...	0.1299	....	....	0.1277	0.1277	0.1266 (10)	None	Slight
5	Hydrazine sulfate 1 +NaBr 1	0.25	...	...	0.1303	....	....	0.1303	0.1303	0.1303 (10)	None	None
5	Hydrazine sulfate 1 +NaBr 1	..	0.124	...	0.1303	0.1303	0.1303	0.1303	....	.....	None	None
Hydrazine Sulfate												
4	......	0.25	...	...	0.1212	....	0.1212	0.1212	....	0 1212 (18)	Light brown	None
2	......	0.25	...	...	0.1009	....	0.1009	0.1009	....	0 1009 (18)	Dark brown	None
2	......	..	0.124	...	0.0908	0.0908	0.0908	0.0908	....	.....	None	None
3	NaBr 1	0.25	...	...	0.1303	....	0.1303	0.1303	....	0.1303 (18)	Light brown	None
2	NaBr 1	..	0.124	...	0.1303	0 1303	0.1303	0.1303	....	.....	None	None
1	NaBr 1	0.25	...	...	0.1303	....	....	0.1303	0.1303	0.1303 (18)	None	None
1	NaBr 1	..	0.124	...	0.1303	0.1303	0.1303	0.1303	....	.....	None	None

* The numbers in parentheses indicate the number of days having elapsed at the time of the last titration.
† Strong odor of aniline.

REDUCING AGENTS

Having demonstrated that nitrates and nitrites cause low results, the next step was to find a method of reduction whereby the arsenic could be accurately determined in the presence of these substances. Experiments were made with various reducing agents and combinations thereof, using in every case 25 cc. each of the standard arsenic solution and nitrate or nitrite solution. The use of a larger quantity of cuprous chloride was first tried, but even 15 g. of this material made practically no change in the results. Ferrous sulfate in combination with cuprous chloride gave distillates which were decidedly yellow, oxidized methyl orange very rapidly, and showed a more rapid decline in the arsenic value than when cuprous chloride was used alone. Rohmer[7] noticed that hydrobromic acid accelerated the reducing action of sulfur dioxide, and attributed to it a catalytic effect. This suggested the use of sodium bromide in combination with cuprous chloride. Distillations made in this way, however, showed only a slight improvement over those made with cuprous chloride alone.

Jannasch and Seidel[8] found that hydrobromic acid together with a salt of hydrazine gave excellent results in the reduction of arsenic. Since hydrazine is such a strong reducing agent it seemed likely that it might destroy the nitrates as well as reduce the arsenic. It was used at first alone and then in combination with cuprous chloride and with sodium bromide. The use of hydrazine sulfate alone eliminated the yellow color and prevented the gradual oxidation of the distillate, but the arsenic was not completely reduced in the time required to obtain 250 cc. of distillate (30 to 40 min.), even when as much as 4 g. of hydrazine sulfate were employed. (This is in accord with the results of Jannasch and Seidel, who found that several hours were required to secure complete reduction by hydrazine sulfate alone.) When the distillations were made with 5 g. of cuprous chloride and 1 g. of hydrazine sulfate the arsenic was completely reduced, but the oxidation of the distillate was not eliminated. When, however, the hydrazine sulfate was increased to 2 g. the oxidation of the distillate was completely prevented. Jannasch and Seidel found that the addition of a bromide to the hydrazine sulfate greatly hastened the reduction of the arsenic, and the writers have found that sodium bromide and hydrazine sulfate when added to the cuprous chloride also completely destroy nitrates. Later experiments showed that equally as good results were obtained without the use of cuprous chloride. One gram of hydrazine sulfate and 1 g. of sodium bromide proved sufficient where the quantity of arsenic pentoxide present did not exceed 0.75 g.

The investigation included some attempts to find a satisfactory substance to destroy the nitrates, which would be cheaper than the hydrazine sulfate. Ammonium chloride and aniline, owing to their known action on nitric acid and nitrites, respectively, were tried but proved to be of no value. The conditions to be fulfilled in this distillation are so circumscribed that the list of possible substances as reducing agents is limited.

RESULTS OF EXPERIMENTS

The results given in Table I show conclusively that, in the presence of nitrates (or nitrites), the distillation method for arsenic as ordinarily carried out, using cuprous chloride or cuprous chloride and ferrous sulfate as the reducing agents, gives low results. This is due to some volatile substance, possibly nitrosyl chloride, carried over in the distillate that oxidizes the arsenic trioxide. The extent of this oxidation depends largely upon the length of time the distillate stands before titration. Where a number of distillations are being carried on at the same time, it is impossible to titrate all of them immediately and the error caused by this oxidation may be a very material one. This error may be avoided by the use of hydrazine sulfate as the reducing agent, or preferably hydrazine sulfate and sodium bromide, in which case the reduction takes place much more rapidly. The nitrates and nitrites are probably reduced to nitrogen by the hydrazine sulfate.

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[7] *Ber.*, **34** (1901), 33.

[8] *Ibid.*, **43** (1910), 1218; *J. prakt. Chem.*, **91** (1915), 133.

Table II—Comparison of Official and Hydrazine Distillation Methods

No.	Material Analyzed	Method of Distillation	Arsenic Oxide Found, Grams: Titrated Immediately	Titrated after 4 Hrs.	Titrated after 1 Day	Titrated after 2 Days	Titrated after 9 Days	Properties of Distillates: Color	Bleaching Action on Methyl Orange at 90° C.
15794	Calcium arsenate	Official	0.1248	....	0.1241	0.1239	0.1231	None	Marked
		Hydrazine	0.1251	....	0.1251	0.1251	0.1251	None	None
15515	Calcium arsenate	Official	0.1242	....	0.1237	0.1234	0.1231	None	Marked
		Hydrazine	0.1246	....	0.1246	0.1246	0.1246	None	None
15468[1]	Calcium arsenate	Official	0.1287	....	0.1287	0.1287	0.1287	None	None
		Hydrazine	0.1293	....	0.1293	0.1293	0.1293	None	None
15792[1]	Calcium arsenate	Official	0.1219	....	0.1219	0.1219	0.1219	None	None
		Hydrazine	0.1222	....	0.1222	0.1222	0.1222	None	None
T 1127	Calcium arsenate	Official	0.1281	0.1270	0.1256	0.1250	0.1237	Yellow	Marked
		Hydrazine	0.1281	....	0.1281	0.1281	0.1281	None	None
T 1128	Calcium arsenate	Official	0.1241	0.1231	0.1210	0.1193	0.1172	Yellow	Marked
		Hydrazine	0.1241	....	0.1241	0.1241	0.1241	None	None
T 1776	Calcium arsenate	Official	0.1099	0.1089	0.1067	0.1053	0.1048	Yellow	Marked
		Hydrazine	0.1101	....	0.1101	0.1101	0.1101	None	None
16333	Lead arsenate	Official	0.1188	0.1185	0.1179	0.1175	....	Very light yellow	Slight
		Hydrazine	0.1188	0.1188	0.1188	0.1188	....	None	None

[1] Contained only a trace of nitrates by phenolsulfonic acid test.

Modified Method[9]

reagents. *Starch Indicator*—Mix about 0.5 g. of finely powdered potato starch with cold water to a thin paste; pour into about 100 cc. of boiling water, stirring constantly, and discontinue heating immediately after the paste is added.

Standard Arsenic Trioxide Solution—Dissolve 2 g. of pure arsenic trioxide in a beaker by boiling with about 150 to 200 cc. of water containing 10 cc. of concentrated sulfuric acid, cool, transfer to a 500-cc. graduated flask, and dilute to the mark.

Standard Iodine Solution—Prepare an approximately 0.05 *N* solution as follows: Mix intimately 6.35 g. of pure iodine with twice its weight of pure potassium iodide. Dissolve in a small amount of water, filter, and dilute the filtrate to 1 liter in a graduated flask. Standardize as follows: Pipet 50 cc. of the arsenic trioxide solution into an Erlenmeyer flask, dilute to about 200 cc., neutralize with sodium bicarbonate, add 4 to 5 g. in excess and add the standard iodine solution from a buret, shaking the flask continuously, until the yellow color disappears slowly from the solution, then add 5 cc. of the starch indicator and continue adding the iodine solution drop by drop until the permanent blue color is obtained. Calculate the value of the standard iodine solution in terms of arsenic trioxide and arsenic pentoxide.

Standard Bromate Solution—Dissolve 1.688 g. of pure potassium bromate in water and dilute to 1 liter. Standardize as follows: Pipet 25 cc. of the arsenic trioxide solution into an Erlenmeyer flask, add 15 cc. of concentrated hydrochloric acid, dilute to 100 cc., heat to 90° C., and titrate with the bromate solution, using methyl orange as indicator. The indicator should not be added until near the end of the titration, and the flask should be rotated continuously in order to avoid any local excess of the bromate solution. The end-point is shown by a change from red to colorless, and the bromate should be added very cautiously when approaching the end of the titration.

Hydrazine Sulfate and Sodium Bromide Solution—Dissolve 20 g. of hydrazine sulfate and 20 g. of sodium bromide in 1 liter of dilute (1:4) hydrochloric acid.

determination—Weigh accurately an amount of the sample containing the equivalent of not more than 0.6 g. of arsenic pentoxide and transfer to a distilling flask. Add 50 cc. of the solution of hydrazine sulfate and sodium bromide and close the flask with a stopper through which passes the stem of a dropping funnel. Connect to a well-cooled condenser, the delivery end of which is attached to the system of flasks described by Roark and McDonnell,[3] omitting the third flask. Boil for 2 or 3 min., then add 100 cc. of concentrated hydrochloric acid by means of the dropping funnel and distil until the volume in the distilling flask is reduced to about 40 cc.; add an additional 50 cc. of concentrated hydrochloric acid and continue the distillation until the contents of the flask are again reduced to about 40 cc. Wash down the condenser, transfer the contents of the receiving flasks to a 1-liter graduated flask, make to volume, and mix thoroughly. Pipet a 200-cc. aliquot to a 500-cc. Erlenmeyer flask, nearly neutralize with sodium hydroxide, finish the neutralization with sodium bicarbonate, add 4 to 5 g. in excess and titrate with standard iodine solution, using starch solution as indicator; or to the 200-cc. aliquot add 10 cc. of concentrated hydrochloric acid and titrate with standard bromate solution, as previously described in this paper.

With a sample equivalent to 0.6 g. of arsenic pentoxide, practically all of the arsenic is distilled over in the first 50 cc. of the distillate, which is a much more rapid volatilization than that which occurs in the official distillation method. A total distillate of 150 cc. is sufficient to insure complete distillation of the arsenic. The method has been applied to the analysis of commercial samples of calcium arsenate, lead arsenate, and other arsenical insecticides containing nitrates, with most satisfactory results in all cases. Table II shows the results obtained by the "official" and by the modified method on commercial samples of lead and calcium arsenates containing nitrates. In the case of the calcium arsenates 1.5 g. of sample were taken for the determination and 2 g. in the case of lead arsenates. The titrations were made on aliquot portions representing 0.3 and 0.4 g. of sample, respectively.

The figures in Table II show that while there is fairly close agreement between the results by the two methods when the titrations are made immediately after distillation, in some instances the official method gives lower results, and when the titration is delayed for several hours the results by the official method are lower in every case. The maximum difference after 9 days amounts to more than 5 per cent of the arsenic present.

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[9] In working out the details of this method it was assumed that commercial calcium or lead arsenates would never contain nitrates in excess of 5 per cent N_2O_5. In the case of mixtures containing more than this amount, the method may require some modification.

Turpentine and Rosin Statistics

The production of naval stores this season (1921-22) up to August 1, according to reports received from producers by the Bureau of Chemistry, United States Department of Agriculture, was approximately 227,000 casks of gum turpentine and 691,000 round barrels of gum rosin. Estimates on production for the balance of the season indicate a probable total production for the entire season of about 427,000 casks of gum turpentine and 1,320,000 round barrels of gum rosin.

Stocks held by producers at the stills on August 1, 1921, show an increase over similar stocks on April 1, 1921, of about 50 per cent. Stocks held by consumers on August 1, 1921, were practically the same as they were on April 1.

Leavens: Their Action and Measurement[1,2]

By Clarke E. Davis[3] and Donald J. Maveety

Research Laboratory, National Biscuit Co., New York, N. Y.

LEAVENING is the process of forming in a dough bubbles of gas which escape in baking and leave a light and porous texture in the baked product. A leavening action takes place when a carbonate or bicarbonate is acted upon by an acid or acid salt. The simplest form of leavening is by the aid of steam. A fairly good result is obtained by baking a mixture of flour and water, where the texture is produced by the escaping steam. The most familiar type of product leavened in this way is army bread or pilot bread.

Soda (sodium bicarbonate) through the agency of heat is a simple form of leavening agent and may be used alone in quantities which will not leave the bad aftertaste due to excess soda. This amount is about 1.5 lbs. sodium bicarbonate per barrel of flour. Ammonium bicarbonate (NH_4HCO_3) and the so-called ammonium carbonate, a mixture of the bicarbonate and the carbamate (NH_4HCO_3 and $NH_4CO_2NH_2$), decompose with heat, liberating ammonia gas and carbon dioxide and thus giving a double leavening value. More complex mixtures are represented by sodium bicarbonate with primary phosphates of sodium or calcium, phosphoric acid, tartaric acid, cream of tartar, sodium aluminium sulfate, etc.

Great confusion prevails as to the chemical reactions which occur when such chemicals are mixed. Hart[4] gives the following reactions:

$$\underset{702}{3\,CaH_4(PO_4)_2} + \underset{672}{8\,NaHCO_3} = \underset{352}{8\,CO_2} + \underset{144}{8\,H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{4\,Na_2HPO_4}$$

$$\underset{188}{KHC_4H_4O_6} + \underset{84}{NaHCO_3} = \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{210}{KNaC_4H_4O_6}$$

Leach[5] gives the following reactions:

$$\underset{234}{CaH_4(PO_4)_2} + \underset{168}{2\,NaHCO_3} = \underset{88}{2\,CO_2} + \underset{36}{2\,H_2O} + \underset{136}{CaHPO_4} + \underset{142}{Na_2HPO_4}$$

$$\underset{188}{KHC_4H_4O_6} + \underset{84}{NaHCO_3} = \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{210}{KNaC_4H_4O_6}$$

$$\underset{150}{H_2C_4H_4O_6} + \underset{168}{2\,NaHCO_3} = \underset{88}{2\,CO_2} + \underset{230}{Na_2C_4H_4O_6.2\,H_2O}$$

Patten[6] gives the following reactions:

$$\underset{702}{3\,CaH_4(PO_4)_2} + \underset{336}{4\,NaHCO_3} = \underset{176}{4\,CO_2} + \underset{72}{4\,H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{480}{4\,NaH_2PO_4}$$

$$\underset{702}{3\,CaH_4(PO_4)_2} + \underset{672}{8\,NaHCO_3} = \underset{352}{8\,CO_2} + \underset{144}{8\,H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{4\,Na_2HPO_4}$$

In order to determine the weight ratios of sodium bicarbonate and the different acids and acid salts, the chemical reactions must be definitely known. In the case of tartaric acid and cream of tartar the reactions needed to be checked for the purposes of the present investigation. In the case of phosphoric acid and primary calcium phosphate some question existed as to the ultimate end of the reactions. The purpose of the writers was to determine the weight of sodium bicarbonate or carbonate which would react with a given weight of phosphoric acid or primary calcium phosphate.

EXPERIMENTAL

TITRATION—Direct determinations of acidity by titration with standard sodium hydroxide gave the following results, in percentages of the acids involved:

	Per cent
Tartaric acid (Phenolphthalein)	99.6
Cream of tartar (Phenolphthalein)	100.4
Phosphoric acid (Methyl orange)	50.0

It was found impossible to analyze primary calcium phosphate by titration.

ELECTROMETRIC TITRATION—The acid reacting substances were titrated electrometrically with standard sodium hydroxide in order to discover any possible irregularities with the different acids. The method and apparatus used were those described by Beans and Oakes.[7] The apparatus was standardized by titration of 0.1 *M* hydrochloric acid with 0.1 *M* sodium hydroxide. (See Fig. 1.) Measurements were made with the same alkali against tartaric acid, cream of tartar, phosphoric acid (commercial), and primary calcium phosphate with the results indicated in Figs. 2, 3, 4, and 5. The curves represent simple electrometric measurements of hydrogen ion designed for comparison with the acidity shown by indicator titration. The abrupt changes in the curves correspond to the sudden changes shown by indicators and represent the end-points of the displacement of a first or second hydrogen. The middle points of the upward breaks represent these values:

	Per cent
Tartaric acid	99.8
Cream of tartar	99.4
Phosphoric acid	52.7
Primary calcium phosphate	86.8

CO_2 EVOLVED—In order to determine directly the weight ratios existing between the carbonate and the acid or acid salt, the weight of carbon dioxide given off by the reactions was measured by means of an absorption train. The reacting materials were weighed into an Erlenmeyer flask, CO_2-free water was added, and the reaction carried to the end by the aid of heat. Sodium carbonate was used because sodium bicarbonate breaks down with heat.

Table I shows the results obtained by actual carbon dioxide measurements.

TABLE I

Acid	Grams	Na_2CO_3 Grams	Measured CO_2 Grams	Theoretical CO_2 Grams
Tartaric	0.5000	0.3516	0.1441	0.1460
Cream of tartar	1.2370	0.3500	0.1440	0.1454
Phosphoric	1.3878	1.000	0.3225	0.3284

Tartaric acid and cream of tartar were mixed with sodium carbonate in stoichiometric proportions. In the case of phosphoric acid, the carbonate was added in excess. These results show the reactions in the cases of tartaric acid and cream of tartar to have been direct neutralization of all the hydrogen ion of the acids. (See equations in introduction.) In the case of phosphoric acid, two-thirds of the hydrogen ion were neutralized and there action came to an end with the formation of Na_2HPO_4, disodium phosphate:

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[1] Presented before the Division of Agricultural and Food Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 3 from the Research Laboratory of the National Biscuit Co.

[3] Consulting Chemical Engineer, National Biscuit Co.

[4] "Leavening Agents," 52.

[5] "Food Inspection and Analysis," 4th edition, 349.

[6] *J. Assoc. Official Agr. Chem.*, **2** (1917), 227.

[7] *J. Am. Chem. Soc.*, **42** (1920), 2116.

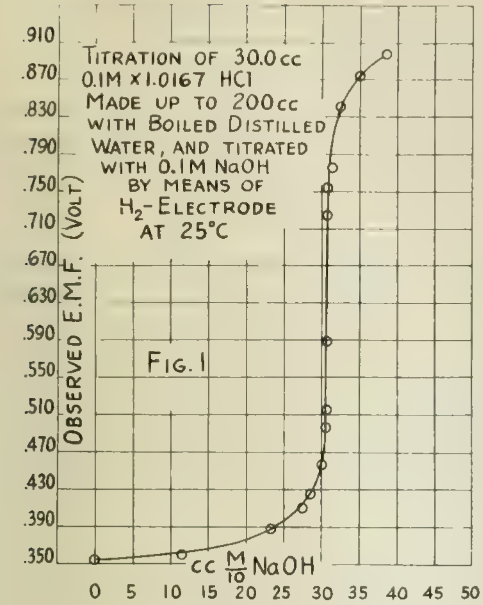
Titration of 30.0 cc 0.1 M × 1.0167 HCl made up to 200 cc with boiled distilled water, and titrated with 0.1 M NaOH by means of H_2-electrode at 25° C

Fig. 1

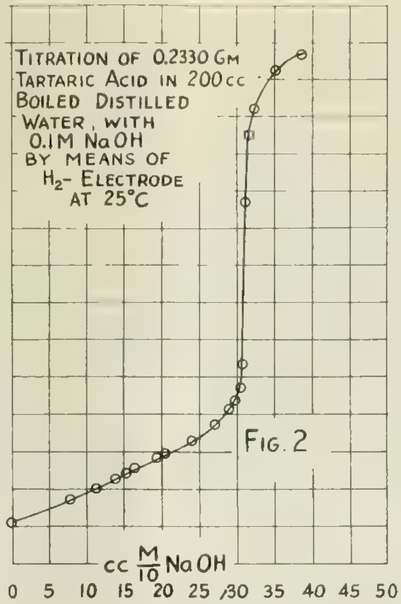
Titration of 0.2330 Gm tartaric acid in 200 cc boiled distilled water, with 0.1 M NaOH by means of H_2-electrode at 25° C

Fig. 2

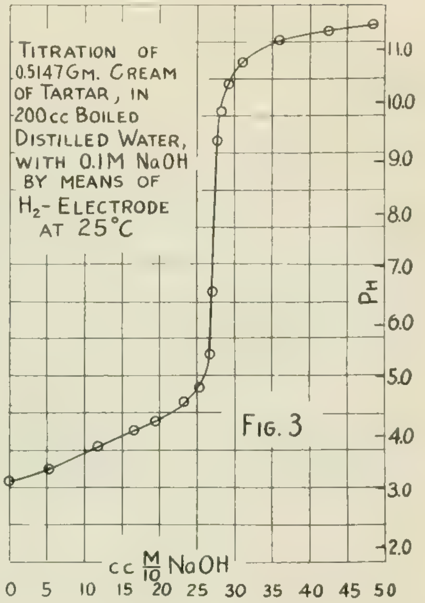
Titration of 0.5147 Gm. cream of tartar, in 200 cc boiled distilled water, with 0.1 M NaOH by means of H_2-electrode at 25° C

Fig. 3

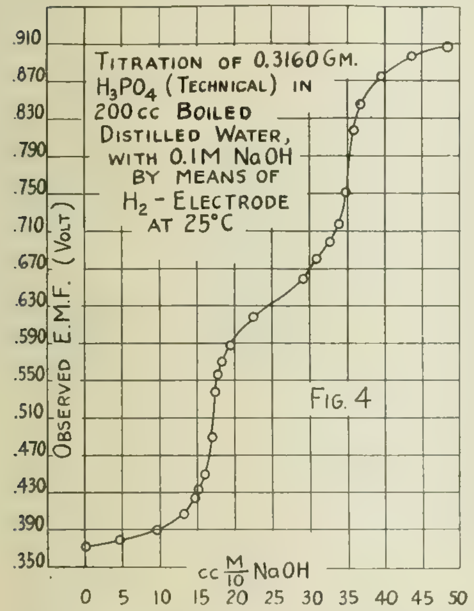
Titration of 0.3160 Gm. H_3PO_4 (technical) in 200 cc boiled distilled water, with 0.1 M NaOH by means of H_2-electrode at 25° C

Fig. 4

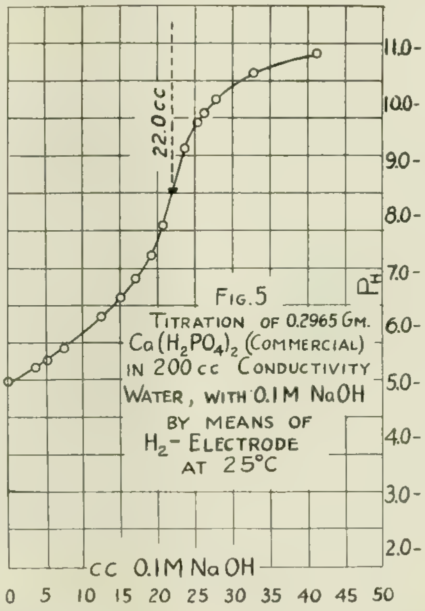
Fig. 5

Titration of 0.2965 Gm. $Ca(H_2PO_4)_2$ (commercial) in 200 cc conductivity water, with 0.1 M NaOH by means of H_2-electrode at 25° C

$$\underset{98}{H_3PO_4} + \underset{106}{Na_2CO_3} \rightleftarrows \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{142}{Na_2HPO_4}$$

Converted to bicarbonate, this equation becomes

$$\underset{98}{H_3PO_4} + \underset{168}{2\,NaHCO_3} \rightleftarrows \underset{88}{2\,CO_2} + \underset{36}{2\,H_2O} + \underset{142}{Na_2HPO_4}$$

When primary calcium phosphate reacts with sodium carbonate, different results are obtained, depending on the ratio of acid to base and on the time of the reaction as indicated in Table II.

Table II

Primary Calcium Phosphate Grams	Na_2CO_3 Grams	CO_2 Produced Grams	Time Hrs.	Theoretical CO_2 Grams
1.000	0.4716	0.1755	1.0	0.1957
1.000	0.4716	0.1920	1.5	0.1957
1.000	1.000	0.2076	1.0	0.2170
1.000	1.000	0.2170	2.5	0.2170

In the first two experiments of Table II the theoretical carbon dioxide was calculated from the amount of sodium carbonate used, and an excess of acid phosphate was present. In the last two the theoretical carbon dioxide was calculated from the acid phosphate used, and sodium carbonate was in excess. This last experiment gave carbon dioxide corresponding to the reaction which has $Ca_3(PO_4)_2$, neutral calcium phosphate, and Na_2HPO_4, disodium phosphate, as its end-products, and did not stop with the formation of $CaHPO_4$, secondary calcium phosphate.

$$\underset{702}{3\,Ca(H_2PO_4)_2} + \underset{424}{4\,Na_2CO_3} \rightleftarrows \underset{176}{4\,CO_2}$$
$$+ \underset{72}{4\,H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{4\,Na_2HPO_4}$$

Converted to bicarbonate, the equation reads

$$\underset{702}{3\,Ca(H_2PO_4)_2} + \underset{672}{8\,NaHCO_3} \rightleftarrows \underset{352}{8CO_2}$$
$$+ \underset{144}{8H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{Na_2HPO_4}.$$

In order to determine whether $Ca_3(PO_4)_2$ or $CaHPO_4$ is formed in a solution which is not strongly alkaline, sodium carbonate and primary calcium phosphate were used in proportions to give the reaction

$$\underset{234}{Ca(H_2PO_4)_2} + \underset{106}{Na_2CO_3} \rightleftarrows \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{136}{CaHPO_4} + \underset{142}{Na_2HPO_4}$$

or, converted to bicarbonate,

$$\underset{234}{Ca(H_2PO_4)_2} + \underset{168}{2\,NaHCO_3} \rightleftarrows \underset{88}{2\,CO_2} + \underset{36}{2\,H_2O} + \underset{136}{CaHPO_4} +$$
$$\underset{142}{Na_2HPO_4}$$

and the carbon dioxide was collected and weighed. The material remaining in the reaction flask was filtered and separate determinations with additional sodium carbonate were conducted on filtrate and precipitate. If carbon dioxide were developed by the action of the solid residue, it would prove that material to be not $Ca_3(PO_4)_2$ but $CaHPO_4$. The results are given in Table III.

TABLE III

	Na_2CO_3 Grams	CO_2 Grams	Calcium Grams	
Primary calcium phosphate 1.171 g.	0.460	0.1845	0.1810	
Filtrate	1.000	0.0477	0.0059	0.1799
Precipitate	1.000	0.0367	0.1740	

Results show that the filtrate contained no appreciable amount of calcium salt. Both the solid and the liquid were acid in reaction, as evidenced by liberation of carbon dioxide upon addition of sodium carbonate. The liquid contained both NaH_2PO_4 and Na_2HPO_4 because the previous experiments showed that with phosphoric acid the reaction could go no farther than Na_2HPO_4, and the development of carbon dioxide in the liquid must have been due to the acid phosphate, NaH_2PO_4. A small amount of calcium existed in solution, probably as $CaHPO_4$. The solid was made up of a mixture of $Ca_3(PO_4)_2$ and $CaHPO_4$. The tertiary phosphate must be present to a certain extent, depending upon the concentration of hydroxyl ion. The intermediate product, the secondary phosphate, will liberate carbon dioxide in presence of carbonate. So, too, would the primary phosphate, but in the presence of the tertiary phosphate the primary would react to form the secondary. To establish the equilibrium there must be present a little primary phosphate. There is a complicated equilibrium in the solution, and between solid and solution, which is disturbed by the action of an excess of Na_2CO_3. Na_2HPO_4 and $Ca_3(PO_4)_2$ are produced in entirety only where a large excess of hydroxyl ions is present.

CONCLUSIONS

1—Results were obtained which give the ratios of sodium bicarbonate and acid leavens to be used for complete neutralization.

2—Electrometric titration curves of some acid leavens have been made.

3—The reaction of sodium bicarbonate and primary calcium phosphate depends upon the concentration of hydroxyl ion present. Liberal excess of sodium bicarbonate causes the tertiary calcium phosphate to form.

Premature Explosions of Nitroglycerin in Oil Well Drilling Operations[1]

By C. W. Porter

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IN the development of oil wells it is often necessary to drive pipes to depths exceeding 3000 ft. Occasionally a pipe is deflected from its vertical course and becomes "stuck." It cannot be driven farther or pulled up. Only one remedy can be applied to save it; the end of the pipe may be shot off by means of a high explosive, such as dynamite or blasting gelatin. It is not uncommon for a charge to explode spontaneously while being lowered. The pipe is then shattered at a point above the source of trouble and the well has to be abandoned. When the shooting is successful, drilling and driving may be continued as if nothing had happened, and the preliminary work (usually representing a value of many thousands of dollars) is saved.

Through the courtesy of the Southern Pacific Co., the writer has had an opportunity to observe operations in the Bakersfield and Coalinga oil fields and to secure data with reference to corrective work elsewhere.

Observations of the most experienced well shooters may be summarized as follows:

1—Premature explosions have not been known to occur in dry wells.

2—In wells filled with water, premature explosions seldom occur at depths of less than 1200 ft.

3—Most premature explosions occur at depths varying between 1600 and 2000 ft.

4—In a few instances detonators have been found intact after the explosions.

5—Explosions have occurred while the charges were in motion, *i. e.*, while being lowered. Others have happened while the charges were at rest, *i. e.*, during the intervals when the machinery was stopped to allow time for lashing to the sand line the insulated wire connected with the detonator.

6—Premature explosions seldom occur when the blasting charges are composed of wrapped sticks of dynamite.

From 4 and 5 it seems evident that the cause of trouble cannot be referred to electrical currents or to friction. It has occurred to the writer that the trouble may be due to the oxidizing effect of air mechanically held within the mass of blasting gelatin.

The shell ordinarily used is a tinned or galvanized sheet iron tube 4 to 6 in. in diameter and 6 to 18 ft. long, closed at the lower end only. By means of a short steel cylinder of the same diameter as the shell, blasting gelatin is cut into pieces corresponding in length to the thickness of the cake of blasting gelatin usually packed for shipment in 50-lb. lots. These pieces are forced into the shell by means of a ramrod. Two or three detonators—all connected to the same wire—are embedded in the mass of blasting gelatin in each bomb. Thin layers of air are held between the separate small units of blasting materials and, very often, pockets containing as much as 25 cc. of air are formed by the introduction of irregular fragments of the gelatin.

The shell is attached to the steel cable used in the drilling process and is lowered rapidly to the place requiring adjustment. The hydrostatic pressure on the gelatin and its imprisoned air is thus changed from 1 atmosphere to 40 or 50 atmospheres within a few minutes. This compression, caused by the weight of water above the charge, not only increases the activity of the oxygen in contact with the gelatin, but simultaneously elevates its temperature. Both effects accelerate the oxidation of nitroglycerin and the oxidation of other components of the mixture. Locally, *i. e.*, in the vicinity of an air bubble, the oxidation may go on rapidly enough to produce the temperature required for detonation.

EXPERIMENTAL EVIDENCE

Some experimental evidence in support of this view has been secured. If the accidents are due to this cause, pure oxygen should be much more active than air and pure nitrogen should be entirely harmless. Ten small glass tubes (1 in. in diameter and 10 in. long) were filled with blasting gelatin in which bubbles of oxygen gas were trapped. Ten other tubes were filled in an atmosphere of nitrogen. The tubes were lowered in an abandoned well 2200 ft. deep, which was filled with water having a temperature of 70° at the 1500-ft. level. Two of the tubes containing oxygen exploded spontaneously—one under 1400 and the other under 1800 ft. of water. The other eight reached the bottom and were brought back to the surface intact. None of the tubes containing nitrogen exploded spontaneously.

The writer believes that many accidents could be averted by replacing the air in shells by an inert gas before introducing nitroglycerin products.

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[1] Received September 19, 1921.

Preliminary Report on Sugar Beets in Louisiana[1]

By C. E. Coates[2] and A. F. Kidder[3]

Louisiana State University, Baton Rouge, Louisiana

A LONG series of results show that it is possible to grow sugar beets of high sucrose and high purity in Louisiana and to obtain heavy yields. This is probably true for the South in general. The best results are obtained by late spring planting. The yields average 18 tons per acre, the purities about 85.0, and the sucrose 14.0. The essential feature is the necessity for obtaining good seed which breeds true to type. Seed grown in the United States to-day fulfils this requirement.

....

The beet sugar industry is in many ways one of the romances of applied science. In 1747 Marggraff of Berlin found 6.2 per cent of sucrose in some beets he had examined. Forty years later Achard, also of Berlin, found that by careful selection of beets he was able to increase the average sugar content considerably, and he established a small factory in 1801, aided by a grant from the King of Prussia.

Since then, beets have been raised in sucrose content from 6 to an average of 15 per cent, occasionally running 18, 20, and even 30 per cent. This has been entirely due to scientific agriculture. From the standpoint of chemical engineering, on the other hand, the manufacturing process has been improved so that now there is a yield of from 250 to 300 lbs. of sugar per ton, together with several valuable by-products. This sugar is chemically pure, without flavor of any sort, and enters the markets of the world in free competition with any other type of sugar. Here then is an industry which has been made possible by scientific agriculture and by applied chemistry working hand in hand, producing an agricultural crop worth hundreds of millions of dollars. There were produced in the United States alone in the year 1919 to 1920, 726,000 tons of beet sugar, which is more than the entire production of cane sugar of the United States with Hawaii thrown in. Not one pound of this would have been produced to-day under the conditions, chemical and agricultural, which existed a century ago. The industry is a magnificient monument to applied science.

SEED SELECTION

All this is well known, but it is necessary to repeat well-known facts in order that one may not lose sight of their significance. In this case, first of all, the sugar content of beets was steadily increased by careful seed selection. The growing of sugar beets for seed is, in reality, a fine art and must be done under the most careful scientific control, but the details of the technic have been mastered and for the last three or four years good beet seed grown in America has been obtainable.

One of the writers (Coates) gave this matter considerable study about twenty-five years ago and in 1899 carried out a series of experiments at the Louisiana State University. It was evident that if beets could be matured in the spring they could be worked into sugar in Louisiana sugarhouses and thus extend the sugar season three months or more. One of the weak points in the Louisiana sugar industry is the fact that the expensive sugarhouses can run only about two months out of twelve. If three months could be added to this, their value would be almost doubled.

The first experiments were made by Coates and Glenk. A commercial variety of Vilmorin Improved was planted in November 1898, and harvested the following May and June (Table I). The results were encouraging, as many beets were found having 14.5 per cent sucrose and a purity of 90. The difficulty was that other beets from the same row had grown so large that in them the sucrose had fallen to less than 9 per cent and the purity to about 70. A careful study of the situation convinced Coates that the beet seeds were not uniform in quality. Some of the beets weighed about 1.5 to 2 lbs. and looked like normal sugar beets, while others, harvested at the same time, were obviously of another variety, mostly mangels which weighed 6 or 8 lbs., or even more, and were low in sucrose. The following year similar experiments were run, from which similar inferences were drawn as to the quality of the seed. In November 1904, Coates made two more plantings, one of Vilmorin Improved, and the other of Klein Wanzleben (Table II). The seed labeled Klein Wanzleben gave beets which were abnormally large and which were low in sucrose. The seed labeled Vilmorin did much better, but this too gave results which were disappointing. It was just possible that these seeds were intentionally mislabeled, as the beet sugar industry in the United States was threatening to be an important factor in the sugar world.

TABLE I

Date of planting, November 10, 1898

Date of Analysis	Average Weight of Beet Grams	Sucrose Per cent	Purity
May 2	600	9.89	73.00
May 3	870	8.13	74.30
May 15	1200	10.76	80.70
May 16	1980	8.59	74.10
May 31	1140	11.54	83.60
May 31	1500	9.49	76.50
June 6	960	12.61	91.30
June 6	930	14.96	90.60
June 10	600	12.64	89.70
May 10	1500	13.64	85.70
June 10	1080	11.99	91.50
June 10	1440	9.24	75.70
June 12	900	12.94	92.40
June 12	630	13.74	84.20
June 12	720	14.04	87.70
June 12	660	11.04	72.10
June 12	4560	8.14	70.70
June 12	2100	8.39	66.30
June 13	480	14.50	90.60

TABLE II—AVERAGE POLARIZATION OF JUICE

	April	May	June	August
Klein Wanzleben.......	5.7	4.8	5.5	3.3
Vilmorin Improved......	9.2	6.8	7.6	7.3

Two years later more plantings were made of Vilmorin and Klein Wanzleben, some November 26, 1907, some January 30, 1908, and a separate lot in August 1908 (Table III). The August seed gave fairly uniform results, high sucrose and

TABLE III—AVERAGE POLARIZATION OF JUICE

Date of planting, November 26, 1910

	April	May
Vilmorin Improved.........	8.50	11.0
Klein Wanzleben...........	7.63	9.6

Date of planting, January 30, 1908

	April	May
Vilmorin Improved.........	6.6	8.9
Klein Wanzleben...........	6.13	7.9

Date of planting, August 31, 1907

	February	April
Vilmorin Improved.........	14.76	10.9
Klein Wanzleben...........	12.88	9.7

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[1] Presented before the Division of Agricultural and Food Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Dean, Audubon Sugar School.

[3] Agronomist and Assistant Director, Louisiana State Experiment Station, Baton Rouge, La.

TABLE IV

					Averages of Weekly Analyses, May 8–July 29					
					May		June		July	
Row	Variety	Source of Seed	Seed Grown at	Calc. Tons per Acre	Sucrose	Purity	Sucrose	Purity	Sucrose	Purity
1	Klein Wanzleben	B. P. I.[1]	Blissfield, Mich.	20.66	13.4	85.0	13.7	86.5	12.50	83.03
2	Alvarado	B. P. I.	Blissfield, Mich.	25.54	14.15	85.98	13.63	83.44	12.06	80.52
3	Klein Wanzleben Elite	B. P. I.	Klein Wanzleben, Germany	20.90	13.4	83.88	14.13	83.21	12.18	81.88
4	Dippe	B. P. I.	Blissfield, Mich.	18.28	14.05	86.15	13.63	83.66	12.40	81.51
5	Jaensch Victrix, 12844	U. E. S.[2]	Logan, Utah	18.52	13.34	84.68	12.80	81.90	10.78	79.29
6	Unnamed	G. W. S.[3]	.....	21.16	14.5	85.65	13.92	80.88	11.92	80.41
7	Unnamed	G. W. S.	.....	17.42	15.16	86.5	14.18	84.74	12.74	81.99
8	Klein Wanzleben	B. P. I.	Blissfield, Mich.	18.72	14.73	85.78	13.62	84.68	13.08	83.66
9	Alvarado	B. P. I.	Blissfield, Mich.	17.22	14.42	86.54	13.41	84.21	11.86	76.29
10	Alvarado	B. P. I.	Blissfield, Mich.	16.70	14.08	85.72	15.16	84.79	12.08	78.75
11	Dippe	B. P. I.	Blissfield, Mich.	16.12	14.52	85.15	14.75	84.67	13.62	84.35
12	Jaensch Victrix, 12844	U. E. S.	Logan, Utah	16.50	13.7	86.59	13.56	83.69	11.96	81.63
13	Unnamed	G. W. S.	.....	19.65	14.49	82.83	14.97	81.66	13.82	83.76
14	Unnamed	G. W. S.	.....	18.65	14.54	84.38	13.50	82.90	12.56	82.33

[1] Dr. Townsend, Bureau of Plant Industry.
[2] Dr. Harris, Utah Expt. Station.
[3] Great Western Sugar Co., Denver, Col.

purity, and normal sized beets in February, but were obviously harvested too late, as is seen in the April figures.

Here again, the beets were so irregular in quality that Coates became convinced it was very difficult to get pure beet seed, and the experiments were discontinued until this important point could be settled.

Most of the previous plantings had been fall planting, which is the custom in Louisiana, and for this reason there was not as much sunshine on the plant when it was approaching maturity as might have been desirable. In fact, beets planted in January contained practically as much sugar in May as did those planted in November. Several sporadic attempts were made in the next ten years, but these developed nothing new, though individual beets were found which gave 20 per cent of sucrose and over.

In 1920, C. E. Coates and A. F. Kidder repeated these experiments, using in this instance late spring planting rather than fall planting. The seed obtained by Kidder was certified to as being pure and true to type. The chemical work was done by Coates and his assistants, the agricultural work by Kidder and his assistants. The results were so exceedingly good that it is thought well to present them in a preliminary form. It must be distinctly understood that this is merely a report of progress. It is the intention of the authors to carry out these experiments over a term of years with annual progress reports.

AGRICULTURAL DATA

The certified seed were furnished by the laboratories listed in Table IV. A fairly uniform plot 42 ft. × 105 ft. was selected for this purpose. The plot was flat broken early in the winter and replowed, disked, and harrowed the 24th of January. Rows were laid off 3 ft. apart with a small middle burster and the seed planted the day the soil was replowed.

The seed came up to an excellent stand and the plants were given the first hoeing on the 25th of February. Other agricultural operations are recorded in Table V.

TABLE V

DATE	Kind of Operation or Work	Cost per Acre
....	Plowing, broadcast	$3.00
January 24	Plowing, disking, harrowing, bedding, planting	4.50
February 25	First hoeing	.40
March 7	Second hoeing and first thinning	2.40
March 17	Cultivated, one horse	.20
March 24	Hoeing and second thinning	2.40
April 4	Cultivated, one horse	.20
May 17	Cultivated, one horse	.20
June 28	Hoeing	1.25
	TOTAL	14.55

This cost does not include harvesting and is not exactly what one would find on a commercial scale, but making all allowances it should not be less than $15 or more than $20 per acre. While it was difficult to calculate yields on the small plots employed, they ran from 16 to 25 tons per acre. There should be no difficulty in reaching the former figures on a commercial scale. The low cost of cultivation is due to the fact that during this particular growing season there is very little trouble from weeds in Louisiana.

Table IV shows the variety, the source of seed, estimated yield, and analytical composition for the three months indicated. Weight of beets, 1.5 to 2.5 lbs.

SUMMARY

1—Sugar beets can be grown successfully in Louisiana, and presumably in the South in general. They can be matured during May, June, and July, and probably during March and April as well.

2—The quality of the beet seed is the vital point. Standard beet seed of high quality is now grown in the United States and would seem to be somewhat better than the best European seed.

3—The tonnage per acre in Louisiana is probably heavier than the average elsewhere, and the sucrose and purity are high enough for commercial purposes. The cost of cultivation is much less than in most beet growing sections.

4—A series of analyses not indicated in these tables shows that the beets after harvesting will keep a week or more without appreciable loss in sucrose or purity. These results are probably too favorable, but it is reasonably sure that after harvesting, beets in Louisiana will not deteriorate more during May, June, and July than will cane in Cuba during the same months.

5—Beets planted on January 24 are ready for harvest by May 8 and probably earlier, and may be harvested in good condition until July 27 and probably later.

American Welding Society Proceedings

The American Welding Society recently issued its first number of proceedings. Beginning with January 1, 1922, the Society plans to issue *Proceedings* monthly in convenient form. In addition to technical papers, the *Proceedings* will include news items and reports of the Society, local sections, the American Bureau of Welding, and the industry. Certain sections will be devoted to editorials, employment service, bibliography of current welding literature, names of new members, etc.

Chandler Medal Award

The lecturer on the Charles Frederick Chandler Foundation this year will be Dr. Edgar Fahs Smith, president of the American Chemical Society. Dr. Smith's subject will be "Samuel Latham Mitchill—A Father in American Chemistry." Samuel Latham Mitchill was the first professor of chemistry at Columbia College and first senator from the state of New York.

The lecture, which is open to the public, will be given on March 2, 1922, at Havemeyer Hall, Columbia University, New York, N. Y.

Effect of Paraffin Wax on the Properties of Mineral Oils[1]

By A. P. Bjerregaard[2]

Research Laboratory, Empire Refineries, Inc., Okmulgee, Oklahoma

PARAFFIN wax decreases the viscosity of the more viscous mineral lubricating oils, raises the freezing point, and lowers the specific gravity. The amount of wax present may be quickly determined, with all necessary accuracy, by observing the freezing point and referring to Graph IIa of the present paper, where the percentage of paraffin wax is plotted against temperature.

Since paraffin wax occurs naturally as a component of many native crude petroleum oils, and therefore also in many intermediate and finished petroleum products, it is of importance to know what influence it exerts on the properties of the various other components of the petroleum, especially those with which it is naturally associated. These are the various viscous and so-called "nonviscous" lubricating oils.

The present study was made from the synthetic viewpoint. Known quantities of components of known properties were mixed, and the viscosity, freezing point, and specific gravity of the mixtures were determined.

Materials Used

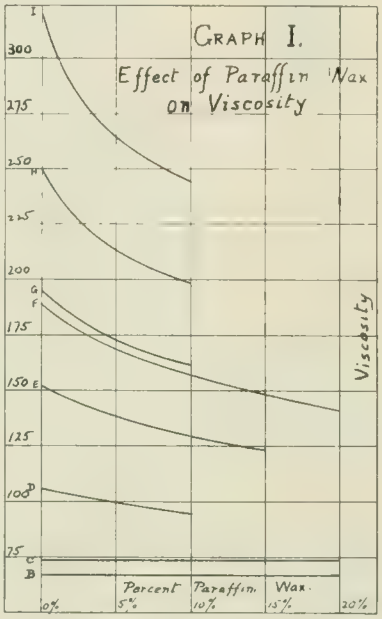
PARAFFIN WAX—Three samples of paraffin wax were used: (1) prepared from Pennsylvania crude oil (nonasphaltic); (2) prepared from mid-continent crude oils, namely, a mixture of Illinois and Healdton crudes (semi-asphaltic); and (3) prepared from a central Oklahoma crude oil (semi-asphaltic).

The first two samples were prepared in the laboratory from "slack wax," which is the raw wax left in the filter presses of the refinery when the wax-containing fractions of the petroleum are filtered at a low temperature, usually about 15° to 20° F. This wax was pressed between blotting papers under a great weight, at a temperature of 80° to 85° F. until no more oil could be extracted. The blotting paper was changed from time to time as necessary. The resulting wax was melted at the lowest possible temperature, and an equal volume of petroleum spirit (usually called turpentine substitute) was added. After slow cooling, the excess of petroleum spirits was poured off, and the paraffin wax pressed as before. Next, the wax was exposed to the air for a short time, until all the remaining spirits had evaporated. The resulting wax was in each case free from oil, and it was not otherwise refined. By the "American method" the melting point of the Pennsylvania wax was 131° F.; that of the mid-continent wax was 130.5° F.

The third sample was a refined commercial wax of 122° F. melting point ("American method"). It was prepared in the refinery in the usual manner, by "sweating" the slack wax and "filtering" or percolating through fuller's earth to remove any color that might be present. The sample contained 1.45 per cent oil.

OILS—The characteristics of the oil samples are tabulated in Table 1.

Effect of Paraffin Wax on Viscosity



The viscosities of varying mixtures of waxes and oils were determined with the Saybolt Universal viscosimeter in seconds at 100° F. All mixtures are stated by weight. The data in Table 2 are plotted in Graph I.

Paraffin wax has no effect on viscosity when this value is low. On the other hand, with oils of higher viscosity, such as the commercial "neutral" lubricating oils, the addition of dissolved paraffin wax decidedly lowers the viscosity. The higher the viscosity the greater the effect of the paraffin wax.

The effect of the paraffin wax is approximately the same as it would have been if an oil of about 70-sec. viscosity had been added instead of the paraffin wax. In other words, the wax acts as a thin oil.

Molten paraffin wax is in fact a thin oil. A sample, like No. 3 of melting point 123° F., "American method," showed a viscosity of 52 sec. at 125° F., and of 46 sec. at 150° F. Calculation from the observed figures to 100° F. leads to approximately 70 sec. for the viscosity of the paraffin wax at 100° F., on the assumption that it were liquid at that temperature.

Table 1—Characteristics of Oils

Oil	Description	Specific Gravity	Viscosity Sec.	Freezing Point ° F.	Color	Fluorescence
A	So-called "nonviscous neutral" oil, from Illinois and Healdton crude oils	0.8665	55	20	Very pale yellow	Blue
B	Pennsylvania "pressed distillate"[1]	0.8534	67	26	Pale brown	Blue
C	Western "pressed distillate"[2]	0.8805	72	25	Brown	Blue
D	Finished lubricating oil, from central Oklahoma crude oil (straight "neutral" oil)	0.8827	106	22	Pale yellow	Bluish
E	Finished lubricating oil (source unknown, but mid-continent) (straight "neutral" oil)	0.8933	152	34	Pale yellow	Greenish blue
F	Finished lubricating oil, from central Oklahoma crude oil (blended "neutral" oil and "cylinder stock")	....	188	..	Red	Green
G	Finished lubricating oil, from central Oklahoma crude oil (straight "neutral" oil)	0.8939	195	24	Red	Bluish
H	Finished lubricating oil, from central Oklahoma crude oil (straight "neutral" oil)	0.8961	249	27	Yellow	Greenish blue
I	Finished lubricating oil, from central Oklahoma crude oil (mixture "neutral" oil and "cylinder stock")	....	320	..	Dark red	Green

[1] This was some of the oil, derived from Pennsylvania crude, which flowed from the filter presses in the refinery during the process of separating the slack wax; in other words, dewaxed wax oil.

[2] Like B, from Illinois and Healdton crude oils.

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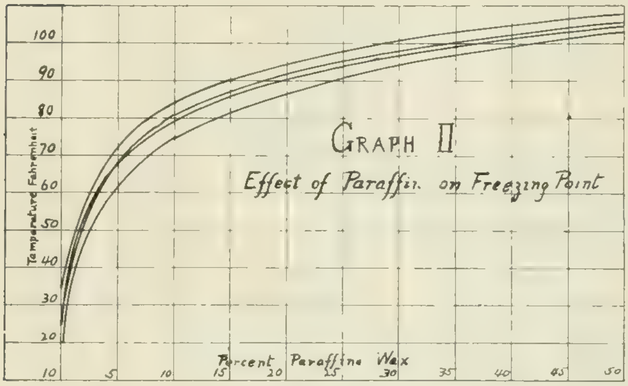
[1] Received September 20, 1921.

[2] Chief Chemist.

TABLE 2—EFFECT OF PARAFFIN WAX ON VISCOSITY

Oil used	B	C	D	E	F	G	H	I
Wax used	1	2	3	2	3	3	3	3
Amount of wax, Per cent								
0	67	72	106	152	188	195	249	320
2	67	73	103	146	...	183	230	...
5	..	73	99	138	...	170	211	...
10	..	73	94	130	158	162	198	244
15	..	73	...	122	...	...	...	...
20	68	73	...	...	141	...	...	...

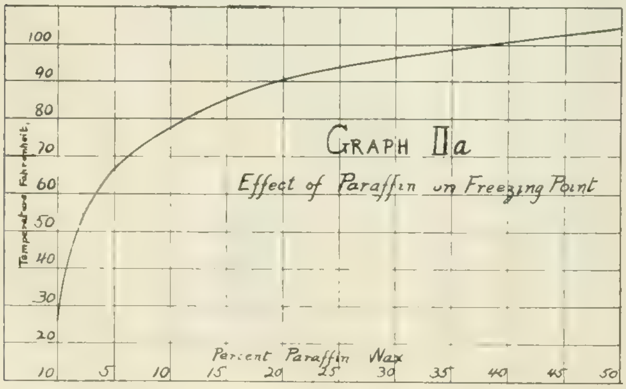


EFFECT OF PARAFFIN WAX ON FREEZING POINT

The freezing points of mixtures of oils and paraffin waxes were determined. The American Society for Testing Materials "Pour Test," D 47-18, was followed except that the actual temperature of solidification was observed and recorded instead of the next higher even 5° or 10° mark.

It may be remarked in passing that this freezing point is not the point of solidification of the whole mass of the oil and paraffin wax mixture, but is due only to the growth of a spongy network of paraffin wax crystals which retains the rest of the oil in its interstices. This is proved by the fact that if the solidified mass, without warming, is stirred, it becomes a liquid with admixed paraffin crystals suspended therein. When this is further cooled it again solidifies, but at a much lower temperature. In this manner, by successive coolings and stirrings, several different freezing points may be obtained with the same solution of paraffin wax in oil. Only the highest solidifying temperature found, without any disturbance of the oil, is considered in this series of experiments.

Table 3 shows the data obtained, some of which are plotted in Graph II.



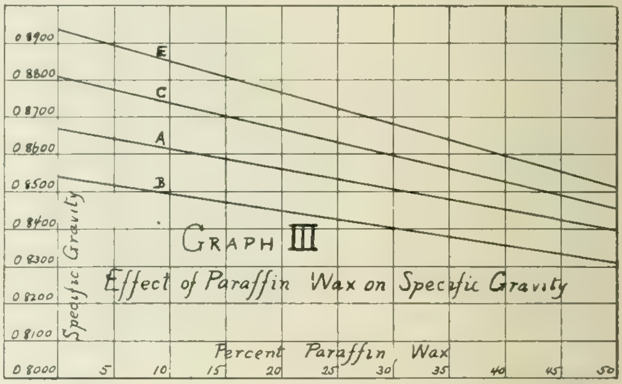
It will be noted that the freezing points of these mixtures do not depend at all upon the kind of oil used. While the freezing point does to some extent depend upon the freezing point of the oil used, the principal factor is the amount of paraffin wax present. Even a very small per cent of the wax causes a large rise in the freezing point. As more wax is added the increment of rise in the freezing point becomes less and less, as indicated in the graph.

TABLE 3—EFFECT OF PARAFFIN WAX ON FREEZING POINT

Kind of oil used	A	B	C	D	E	G	H	
Kind of wax used	2	1	2	3	2	3	3	
Amount of wax Per cent								Av.
0	20	26	25	22	34	24	27	26
2	47	50	55	50	55	52	50	51
5	63	69	68	64	73	66	65	67
10	75	81	79	74	84	75	73	77
15	81	86	85	..	89	..	..	85
20	87	91	91	..	94	..	..	91
25	91	95	93	..	98	..	..	94
50	103	106	105	..	108	..	..	105

The freezing points (before adding the paraffin wax) of the oils used are dependent on the amount of paraffin wax left in them by the manufacturing operations. It is possible to reduce them all to the same basis by simply shifting the location of the starting points on the graph all to the same place. The other end of the curve must not be shifted, because the wax is assumed to be the same in each case. Hence the curve will be shifted in a rotational way with the 100 per cent wax point as the center.

If by this means all the data be reduced to a common starting point, say at 26° F., the freezing points of all the oil and paraffin mixtures will fall on the same curve, within the limits of experimental error. This is virtually the same as making the assumption that all the oils used had originally a freezing point of 26° F., before adding the paraffin wax. The curve thus obtained is practically identical with that derived from the arithmetic averages of the freezing points for the mixtures with the same wax content. Such a curve is plotted in Graph II*a* and the figures are shown in the last column in Table 3.



Graph II*a* has been found very useful in the examination of wax distillates for paraffin wax content. Instead of the time-consuming and inaccurate Holde method of estimating the wax content, all that is necessary is to determine the freezing point and refer to the curve of Graph II*a*. Thus, if the freezing point is 70° F., there is a wax content of 6.5 per cent together with 93.5 per cent of oil of 26° F. freezing point. The writer has used this method for the past five years and has found it sufficiently accurate and reliable for all practical purposes.

EFFECT OF PARAFFIN WAX ON SPECIFIC GRAVITY

The specific gravities of mixtures of paraffin wax and oils were determined by means of a hydrometer, while the mixture was warm enough for all the wax to be in clear solution. In Table 4 these determinations have all been reduced to their equivalents at 60° F., by means of the tables commonly employed for that purpose in the petroleum industry.

Graph III (plotting the data of Table 4) shows clearly that the specific gravity becomes smaller with the addition of paraffin wax to the mineral oil, the more rapidly the heavier

Table 4—Effect of Paraffin Wax on Specific Gravity

Kind of oil used . .	A	B	C	E
Kind of wax used .	2	1	2	2
Amount of wax Per cent				
0	0.8665	0.8534	0.8805	0.8933
2	0.8654	0.8529	0.8800	0.8922
5	0.8639	0.8514	0.8772	0.8888
10	0.8618	0.8498	0.8745	0.8838
15	0.8591	0.8478	0.8702	0.8805
20	0.8550	0.8448	0.8654	0.8755
25	0.8519	0.8423	0.8628	0.8718
50	0.8398	0.8304	0.8453	0.8519

the original oil. The fact that the graphs are all straight lines shows that there is no change of total volume when the paraffin wax is dissolved in the oil. In this respect paraffin wax behaves like any liquid mineral oil.

Summary

1—When paraffin wax is added to mineral lubricating oils it decreases the viscosity of the more viscous oils, but not of the less viscous ones.

2—Paraffin wax in solution in mineral lubricating oils acts like a thinly fluid oil, so far as its effect on the viscosity is concerned.

3—The addition of paraffin wax to mineral lubricating oils raises the freezing point according to a definite relationship, dependent solely on the amount of paraffin wax present.

4—A quick and easy way of determining the amount of paraffin wax in waxy oils, to a sufficiently accurate degree for all practical purposes, is pointed out.

5—Paraffin wax lowers the specific gravity of mineral lubricating oils. The graph showing this relationship is a straight line. Hence there is no change of total volume on dissolving paraffin wax in mineral lubricating oils.

Acknowledgment

Part of the work herein recorded was done in the laboratory of the Canfield Oil Co., at Cleveland, Ohio, and part was done in the laboratory of the Empire Refineries, Inc., at Okmulgee, Okla. The writer's thanks are here expressed to the respective managers of these companies for permission to publish these data.

Manufacture of Chemically Pure Dextrose[1]

By Chr. E. G. Porst and Nicholas V. S. Mumford

Corn Products Refining Co., Edgewater, New Jersey

The following paper describes the development of the process by which chemically pure dextrose is now manufactured on a commercial scale for medical use.

UP to a short time ago, chemically pure dextrose was used only for laboratory purposes and in small amounts. Several years ago, however, several physicians, individually, began to see possibilities in the use of chemically pure dextrose for medical purposes, and this laboratory was requested to furnish what, at that time, was a fairly large amount.

The Earlier Methods

The method used at first was essentially that described by R. F. Jackson,[2] in which alcohol was used as a washing medium and as a precipitant for dextrins. By this means a 99.9 per cent dextrose was obtained from "Cerelose,"[3] but the use of large quantities of alcohol made the method too expensive for practical use.

A method suggested by Mr. C. S. Hudson of the Bureau of Chemistry, involving the use of glacial acetic acid in the ratio of one part of acid to one part of a 70 to 75 per cent solution of dextrose, was tested out. There was, however, danger of some acid being left in the final product, and since the cost of production was also high the method was abandoned in the experimental stage.

The method which was successfully used for two years or more involved solution of Cerelose in water to a density of about 63° Brix, treatment of this solution at 70° to 80° C. with from 0.5 to 1.0 per cent of "Eponite," filtration through a glazed stoneware Büchner funnel, crystallization in 10-gal., glazed stoneware crocks, and centrifuging. On re-solution and retreatment with Eponite a sugar was obtained which gave no test for dextrins and contained less than 0.1 per cent ash. A third recrystallization was usually made to insure the complete removal of dextrins, but it was not possible to reduce the ash content much below 0.05 per cent.

When, however, it became necessary to turn out C. P. dextrose at the rate of 200 lbs. per week, this process was not practicable. Sufficient Eponite could not be obtained and the capacity of the Büchner funnel was not great enough to handle the solutions. Furthermore, the number of crystallizations, which were the time-consuming factor, must be reduced.

Improved and Simplified Method

For the decolorizing, two small boneblack filters, connected in tandem, were connected with a barrel which would give a 5-ft. head. These filters were filled with activated boneblack and the solutions were run by gravity through both of them. Except when the liquors had been excessively overheated in making them up, this treatment gave a clear, water-white solution for crystallization. When the solutions were not clear or white, the liquor was passed through the filters over fresh boneblack a second time before it was allowed to crystallize.

In order to reduce the number of crystallizations, the Cerelose was mixed for half an hour in a kneading machine with enough water to give a mixture which could be handled in the centrifugal. No definite ratio of water to Cerelose was adopted, because the amount of water necessary varied considerably, depending on how long the Cerelose had aged before being pressed and on how much pressure had been used. This treatment served to remove some of the color and also a considerable proportion of the impurities, the purity being raised to 99.0 per cent.

This magma was spun as dry as possible and the sugar obtained was melted with enough water to give a solution of from 63° to 68° Brix, depending on the temperature out of doors. The melting was done in the barrel which supplied the boneblack filters, the barrel being fitted with a steam coil and an air agitator. Thirty to forty gallons of solution were made up at a time.

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[1] Presented before the Division of Sugar Chemistry and Technology at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Bur. Standards, *Sci. Paper* 293.

[3] "Cerelose" is a corn sugar, made by allowing a highly converted corn sirup to crystallize, cutting the resulting mass into slabs, pressing out the mother liquor ("Hydrol"), and drying the pulverized cake. The sugar thus obtained is a light yellowish brown, granular substance of about 96 per cent purity.

Before starting the liquor through the boneblack filters the water in the jacket surrounding them was heated to 70° to 80° C. and the temperature of the liquor was held at the same figure. On starting the liquor through the filters, it was invariably found that there was a certain amount of moisture in the bone which was displaced by the liquor. The liquor leaving the filter for the first 10 to 15 min. was, therefore, caught in a pail and returned to the barrel to be refiltered. When the gravity rose to the desired degree, the liquor was turned into 10-gal., glazed stoneware crocks. The density of the liquor in each crock was tested when full and adjusted to the value needed for that day's work by the addition of water. This adjustment was allowed for by making the density of the solution in the barrel slightly higher than that desired for crystallization. If the density was too low, it was necessary to return the liquor to the barrel, add more sugar, and run it through the filters again.

The liquor was allowed to stand without disturbance in the crocks. No seed was added, as it was found that seeding caused too rapid crystallization, giving fine crystals which went through the screen of the centrifugal. As the liquor cooled down, crystallization set in and the crystals sank to the bottom, increasing in size as they dropped. Ordinarily crystallization was complete, as determined by the temperature of the massecuite approaching that of the room, in from 48 to 72 hrs. Occasionally, however, owing to sudden changes in the weather from cool to very hot, the crystallization did not proceed after a layer of crystals an inch or so thick had settled to the bottom of the crock. It was then necessary to stir these crystals up; otherwise they would grow together, forming large lumps which could be broken up for treatment in the centrifugal only with great difficulty. After stirring, the crystallization proceeded very rapidly, being complete in another 12 to 24 hrs. The crystals very often grew to a length of 0.25 in. or more, but they were so soft that it was never found possible to separate any of this size, for they were broken up in transferring them from the crock to the centrifugal. However, they did not break up sufficiently to cause trouble by passing through the screen of the centrifugal.

When the massecuite was ready for swinging, it was stirred up in the crock as completely as possible, to break up lumps. The centrifugal used both for the massecuite and the magma of Cerelose and water was a 15-in. basket, underdriven machine, designed to turn at 3000 r. p. m. Owing to the difficulty experienced in starting up the machine when loaded, it was never driven over 1500 r. p. m. It was driven at about 900 to 1000 r. p. m. until practically all the mother liquor was out; then it was stepped up to full speed, and the wash water was added from an ordinary laboratory wash bottle fitted with a rubber tube so that the stream could be moved up and down over the whole depth of the basket.

The machine was kept running until practically no more wash water was running off, usually about half an hour. If the time went over three-quarters of an hour, it was judged that the crystals were too small and closely packed for good washing and the crock was remelted, run through the filters, and recrystallized.

The dry sugar, containing 20 to 30 per cent of moisture, was broken up by hand on trays, which were put in an air dryer from which dust was excluded as effectively as possible. The dryer was maintained at a temperature of 40° to 50° C. Although R. F. Jackson states that the crystal water of dextrose hydrate is given off at 60° C., no difficulty was experienced in reducing the moisture content of the dried sugar to less than 1 per cent at this low temperature.

The dried sugar, which had sintered slightly, was passed through a Mead mill to reduce it to a powder. Unless the dextrose was almost bone-dry the mill clogged up badly. Previous attempts to grind dextrose in a ball mill had given the same result. Owing to the amount of dextrose that did stick to the beaters and bars of the Mead mill, it was certain that sugar passing through did not pick up any impurities from the mill.

The dextrose obtained by this single crystallization had a purity of 99.90 to 99.95 per cent and was sufficiently pure for the purpose of milk modification for baby-feeding experiments, for which it was chiefly used. If a still higher purity was desired, as when the sugar was to be used for intravenous injection, another crystallization was made.

Preparation from "Refined Cerelose"

This process was continued until the new process of making high purity dextrose, developed by Dr. Chr. E. G. Porst and Mr. W. B. Newkirk, was put into operation. The use of the kneading machine was then abandoned and the high purity dextrose or "Refined Cerelose" is now melted and run through the boneblack filters. As the purity of the original dextrose is 99.0 per cent or better, a single crystallization is sufficient to give a product of 99.9 per cent purity, and a second crystallization gives a product whose purity can be improved only by the use of the most refined methods of purification.

International Conference of Chemistry

The International Union of Pure and Applied Chemistry announces that the next international conference will be held at Lyons June 28 to July 1, 1922. The International Commission on the Elements, discussed at the Brussels meeting, has been organized and will present its first report at the Lyons meeting. By unanimous vote the commission has agreed to the creation of three subcommittees (isotopes, radioactive elements, atomic mass). It has been decided to appoint three international commissions of nomenclature: (1) organic chemistry; (2) inorganic chemistry; and (3) biological chemistry. The Commission on Unification of Bibliographic Abbreviations, named at Brussels, recommended the system of abbreviations employed in *Chemical Abstracts* and the Bureau of the Union has decided to conduct an investigation to see whether the principal chemical periodicals will be willing to adopt this system of abbreviations.

Other questions taken up at Brussels and to be again considered at Lyons are: unification of chemical abstracts; international institute of chemical standards, of which there are three sections (bureau of physicochemical standards at Brussels; pure products for research in England; and service of documentation on industrial and technological products in Paris); international laboratory of analysis of food products, for the installation of which the French government has already provided; and the creation of laboratories fo the study of ceramic products and combustibles.

The Bureau of the Union would welcome suggestions as to what questions this country desires to have discussed, and in order that suitable arrangements may be made for the proper presentation of the subjects requests that replies be submitted before April 1, 1922. The Bureau urgently requests that each adhering country pay its subscription promptly.

In the arbitration of the Tacna-Arica controversy between Chile and Peru, the possibility is presented of Chile's losing the potentially valuable Chilean nitrate beds located in the territory under discussion. Bolivia has indicated that she should be included in the parley because Chile's title to the western seacoast was obtained in 1904 through a treaty executed under duress. Chile declares that Bolivia was paid £6,000,000 for her coastal territories, and that she will not enter the conference if Bolivia is admitted. The territory in question involves provinces at the northern end of Chile, one or two of which are said by government experts here to contain valuable nitrate beds.

An Unusual Type of Casinghead Gasoline[1]

By C. E. Coates[2] and B. Y. Tims

Louisiana State University, Baton Rouge, Louisiana

Gas from the Terrebonne Gas Field, about twenty miles below Houma, La., is piped to the town for use as a fuel. The condensate which forms in the pipes is the subject of the investigation recorded in this paper. It differs from ordinary casinghead gasoline in boiling point and other properties. Fractional distillation gives products of fairly constant boiling points, the lowest fraction having the formula $C_{12}H_{22}$. The condensate contains no paraffin hydrocarbons and is probably made up of dicyclopentyl, $C_{10}H_{18}$, and its homologs.

The gas wells of Louisiana, and for that matter, gas wells in general have, during the last few years, been yielding, not only gas, but a fairly large quantity of a very light gasoline. The amount of this gasoline depends upon the nature of the gas, that yielding very little being called dry gas; that yielding considerable being called wet gas. It is commercially profitable to extract this gasoline down to a certain minimum content. Extraction was formerly accomplished at the well by compressing the gas, cooling the compressed gas, drawing off the condensed gasoline and allowing the remaining gas to expand around tubes containing the incoming gas, thus cooling the latter. This process took place at the head of the well, and the product was hence called casinghead gasoline. At present it is considered cheaper to pass the wet gas through a heavy nonvolatile mineral oil, which absorbs the gasoline and from which the gasoline may be subsequently recovered by steam distillation, the oil being returned to process. This casinghead gasoline is exceedingly volatile, and is ordinarily mixed with somewhat high gravity gasolines, in order to make them more readily ignited in an internal combustion engine.

The only considerable deposits of gas in South Louisiana occur in the Terrebonne field, located about twenty miles south of Houma. In this field three producing wells have been, for a number of years, delivering gas at a pressure of about 1200 lbs. per sq. in. at the well. This gas is carried by pipes to Houma and its vicinity, and to the various sugarhouses in that section. The gas appeared to be wet, because quantities of a liquid condensed in the pipes in Houma and had to be collected in drips and removed at intervals. This liquid was considered casinghead gasoline, and was mixed with ordinary gasoline for use in automobiles in Houma. It, however, showed certain properties not possessed by ordinary gasoline, and for this reason Dr. C. M. Menville, at the request of Dr. Coates, collected and sent to his laboratory about 2 gal. of the crude condensate.

Physical Properties

The oil was light in color and slightly fluorescent, and had an odor like pine oil, or oil of cedar. On analysis it gave values listed in Table I.

Table I

Refractive index at 17° C. = 1.4590
Specific gravity = 0.84819 at 24.5° C./24.5° C.
Flash point = 61° C.
Burn point = 63° C.
Cold point = below −7° C.
Viscosity at 25.5° C. = 1.22
B. t. u. = 19.363
Per cent sulfur = 1.09

The flash point determination was carried out in an open cup, heat was applied very gradually, and the process repeated a number of times.

In burning, the gasoline gave off heavy, black smoke with an unpleasant odor.

The heating value of the gasoline was determined in an Emerson bomb calorimeter. Sulfur was determined from the washings of the bomb.

Distillation

For the distillation, 500 cc. of gasoline were taken. Vaporization began at about 50°, and actual distillation at about 94° C. Only a few cubic centimeters came over between 94° and 100° C. The temperature then rose suddenly to 195° C., after which the distillation proceeded steadily. The distillate was collected in 2° fractions. All the fractions were colorless except the last two, which were slightly fluorescent. A small amount of tarry matter remained in the flask after distillation was complete. At 226° C., heavy yellow fumes were given off and no more distillate came over. Table II gives the results of distillation.

Table II—Fractions of Distillate (Atmospheric pressure)

° C.	Cc.
Below 195	2
195–200	50
200–202	65
202–204	62
204–206	64
206–208	54
208–210	50
210–213	50
213–217	50
217–220	24
220–226	27
Total	498

The fractions were purified by shaking with concentrated sulfuric acid, separating the oil, washing with water, shaking with sodium carbonate, decanting, and removing the excess water with powdered calcium chloride. The acid treatment removed a considerable amount of tarry matter. After purification, the turpentine-like odor of the original gasoline was greatly lessened, although it persisted in spite of acid treatment and subsequent redistillations.

Refractionation—The fractions, after purification, were distilled separately. The temperature of distillation varied in each case from 10° to 30° C. from that of the distillation temperature of the fraction. For lack of time, only the first three fractions, 200° to 202°, 202° to 204°, and 204° to 206° (in all 100 cc.), were redistilled in this way in a 200-cc. flask. As distillation in all cases seemed to cause a slight decomposition, it was carried on in this case under a vacuum of 61 mm., but even here there was decomposition. About 20 cc. of a brown liquid remained, but the fraction coming over from 207.5° to 209.5° C. was water-white and was taken for the subsequent work. It still had the odor of cedar or pine oil and contained no sulfur. Treated with bromine at the laboratory temperature of 25°, it seemed to behave as a saturated compound. Upon redistillation at 61 mm., it gave a water-white fraction for which the analytical results in Table III were obtained. For sake of comparison, they are tabulated against some figures obtained by Coates, who was working on a fraction obtained from the Jenning oil. In calculating molecular refraction, the formula of Lorentz and Lorenz was used.

From these data it will be evident that this condensate

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[1] Presented before the Section of Petroleum Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

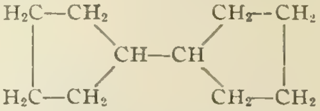
[2] Dean of Audubon Sugar School, and Head Professor of the Department of Chemistry.

TABLE III

	Coates	Coates and Tims
Formula	$C_{12}H_{22}$	$C_{12}H_{22}$
Molecular weight, calculated	166	166
Molecular weight, found	167	167
Carbon, calculated	86.74	86.74
Carbon, found	86.68	86.30
Hydrogen, calculated	13.26	13.26
Hydrogen, found	13.43	13.50
Specific gravity	0.8511 28°/4°	0.84819 24°/24°
Boiling point, 760 mm.	215°–217°	215°–217°
Refractive index	1.4640, 25° C.	1.4546, 29° C.
Molecular refraction, calculated	53.13	53.13
Molecular refraction, found	53.48	53.24

does not resemble in the least the ordinary casinghead gasoline. Its boiling point is far too high, as is also its specific gravity. A study of the particular fraction boiling from 215° to 217° shows it to be identical with a fraction obtained by Coates and his assistants in 1906 from the crude oil in Jennings, La.[3]

Schmidt and Sigwart[4] have identified the series $C_{10}H_{18}$ and its homologs found in Louisiana petroluem by Coates as being dicyclopentyl



and its methyl derivatives, which they made synthetically. The compound $C_{12}H_{22}$ would, therefore, be the dimethyl derivative. The higher and lower derivatives were also isolated by Coates from the South Louisiana petroleums and occur in this condensate as well.

This would indicate that inasmuch as the gas deposit at Terrebonne carries a condensate which is identical with that obtained at Jennings, the two deposits are probably similar in formation. It might also be a slight indication of the presence of an oil pool in Terrebonne, similar to that which has been found in Jennings.

[3] *J. Am. Chem. Soc.*, **1906**, 384.

[4] *Ber.*, **1912**, 1779.

Determination of Volatile Combustible Matter in Pitch Coke[1]

By H. E. Lloyd and F. W. Yeager

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Within a comparatively recent period pitch coke has found use in the manufacture of electrodes, and in certain metallurgical processes where a low volatile coke of high purity is required. Since only a coke of very low volatile content possesses sufficient conductivity to be suitable for electrode use, the accuracy of the determination of volatile combustible matter (V. C. M.) in this class of material takes on new significance.

The work described in the following paper indicates that variations in these analytical results are due to variations in the type of crucible cover used, the weight of sample, the size of crucible, and the method of calculating results. The method which gives the more accurate results, particularly with low volatile cokes, follows the procedure given in test A. S. T. M. D-37-18 under the determination of volatile matter in coke, with the exception of the use of a 2-g. sample and a second 7-min. heat correction.

CERTAIN factors operative in the determination of V. C. M. in pitch coke are particularly likely to affect the accuracy of the results on account of the low volatile content of the material. Considerable work has been done on this test, but the inaccuracies possible seem not to be generally recognized.

The authors had occasion to determine the V. C. M. of pitch coke by two different methods, the differences in which are listed in Table I. The coke was ground in porcelain to pass a 60-mesh sieve.

TABLE I—DIFFERENCES IN METHODS

	METHOD I	METHOD II
Type of crucible	Usual shape; capacity 20 cc.; lid of usual flat type	Capsule shape; capacity 10 cc.; lid tight-fitting inside crucible
Weight of sample	1.000 g.	2.000 g.
Manner of heating	Bunsen flame 20 cm. long (temperature 900°–950° C.)	Electric furnace 950° C. (A. S. T. M. D-37-18)
Time of heating	One 7-min. period	Two intermittent 7-min. periods
Calculation of results, giving V. C. M. as:	Loss in weight reported in per cent of sample weight	Loss on second heat subtracted from loss on first heat and remainder reported as per cent of sample weight

Method II, which is being used by the Aluminum Company of America for certain types of low volatile coke, has for its purpose a correction for the oxidation of the nonvolatile portion of the coke encountered during the first period of heating. This correction is based on the loss found on a second 7-min. heating. The use of a second heating correction factor was suggested by Meade and Attex,[2] who have shown that results so corrected approximate very closely the loss on heating in an inert gas.

Two samples of coke gave results listed in Table II.

TABLE II—PERCENTAGE OF VOLATILE COMBUSTIBLE MATTER[1]

SAMPLE	Method I	Method II	Ratio I:II
1	2.3	0.3	1:0.13
3	6.1	3.5	1:0.57

[1] All figures reported are the averages of two or more check results.

Considering the wide differences in methods used, the basic reasons for such results are apparent. However, the reason for the marked disproportion between the results on cokes of different volatile content as indicated by the ratios in Table II is not so evident.

A brief review of the literature shows that the loss due to oxidation by the air remaining in the large type of crucible was early investigated. To minimize this loss Shimer[3] proposed the use of two 15-cc. platinum crucibles, one fitting tightly within the other with the sample between. Meade and Attex[4] recommended making the test in an atmosphere of nitrogen. Shimer suggested the addition to the sample of alcohol, and Parr[5] of kerosene, for the same purpose. The variations in V. C. M. tests due to mechanical losses, variations in heat, type of crucible, character of flame, type of burner, etc., have been discussed by Parr.[6] Fieldner and Davis[7] have studied the influence of gas pressure, swelling of coal, type of burner, and condition of crucible, *i. e.*, dull

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[1] Received June 20, 1921.

[2] *J. Am. Chem. Soc.*, **21** (1899), 1137.

[3] THIS JOURNAL, **1** (1909), 518.

[4] *J. Am. Chem. Soc.*, **21** (1899), 1116.

[5] THIS JOURNAL, **3** (1911), 900.

[6] *Ibid.*, **4** (1912), 352.

Ibid., **2** (1910), 304.

or bright. Fieldner[8] determined the effect of change of temperature and of type of crucible.

In the present investigation attention was first given to the influence of a change in sample weight.

Change in Sample Weight

Sample 3, Table II, was used for the tests. Table III shows the results obtained in the electric furnace with both types of crucible, each with 1- and 2-g. samples.

Table III—Percentage Lost with Samples of Different Weight

	Weight of Sample	
	1.000 Gram	2.000 Grams
	10-cc. Crucible (Capsule Type)	
1st heat, 7 min.	4.21[1]	3.99
2nd heat, 7 min.	0.79	0.53
	20-cc. Crucible	
1st heat, 7 min.	5.25	4.55
2nd heat, 7 min.	2.17	1.19

[1] This result is by A.S.T.M. Method D-27-18 in all respects.

In every case the per cent loss in weight, irrespective of the size of crucible, is greatest where the sample is smallest. The cause for this is thought to be the variation in the depth of coke layer; in other words, the relative coke contact surface per gram of sample which is dependent upon the sample weight. This difference has an appreciable effect where the same crucible is used, but where the 2-g. sample is charged to the 10-cc. capsule and a 1-g. sample to the 20-cc. crucible, the difference in coke contact surface between the two combinations is considerable. Parr[6] regards variation in this contact surface as affecting the results of tests to a considerable degree, the cause being, in his opinion, the effect of differences in coke contact surface per gram on the speed with which the heavier volatile constituents are discharged.

The losses for the second period heats are due mainly to oxidation of the coke residue remaining after the first heat, either by the air in the crucible or that entering during the second heat. Under these conditions the coke contact surface is of less importance as a factor affecting the per cent loss and while the per cent loss is different the actual weight loss tends to be approximately the same for each crucible, respectively.

Type of Crucible

The data obtained in the above tests also serve to show the difference due to the type of crucible.

With the same weight of sample the loss is greater when the 20-cc. crucible is used. This may be attributed to two factors, (1) size of crucible, and (2) type of cover.

In their entirety these results show that the difference between the two methods as to type of crucible and amount of sample tend to produce a lower percentage loss in weight in Method II. When this difference in actual per cent loss is augmented by the correction in Method II which further reduces the figure for V. C. M., it is readily apparent that in any case lower results are inherent in Method II than in Method I.

However, these data do not account for the disproportionate results obtained in different cokes. The cause for this difference, as shown by Table IV, does not lie in the calculation of results, but is operative during the first 7-min. heating of the crucibles.

Table IV—Loss on First 7-Min. Heating

(Sample 1, low volatile coke; Sample 3, high volatile coke)

	Method I		Method II	
	Sample 1 *a*	Sample 3 *b*	Sample 1 *a*	Sample 3 *b*
Weight loss, gram	0.0225	0.0608	0.0109	0.0789
Per cent loss	2.25	6.08	0.55	3.99

Here the relation represented by b in terms of a is, for Method I, $b = 2.7\ a$; and for Method II, $b = 7.2\ a$.

It appears that the cause for this variation can be traced to some difference of conditions which permits unequal degrees of oxidation or combustion with respect to high and low volatile cokes in the two methods, such as (1) fit of crucible lids, (2) difference in relation of air volume to coke sample weight, or both.

Type of Crucible Lid

The effect of a loose-fitting lid was tried out on the 10-cc. crucible with a 2-g. sample. A comparison of these results with previous ones using the usual tight lid is made in Table V.

Table V—Effect of Type of Crucible Lid

(Per cent loss, 1st heat, 7 min., furnace 950° C.)

	Sample 1 *a*	Sample 3 *b*	*b/a*
10-cc. crucible, usual tight lid..............	0.55	3.99	7.2
10-cc. crucible, loose lid...................	1.23	4.48	3.6
20-cc. crucible, flat lid....................	2.25	6.18	2.7

These results indicate that the relative tightness of the lids, of necessity causing a difference in amount of oxidation, is closely connected with the variation of the relation between the high and low volatile coke tests; particularly when it is seen that, not only is there an increase in loss in each case when the loose lid is used, but this increase is different for cokes of different volatile content, and brings the ratio of their apparent V. C. M. to a figure approximating the ratio obtained by the 20-cc. crucible method (see *b/a*).

Explanation of Results—The explanation of the discrepancy in results of the two methods with samples of high and low volatile coke may be as follows: In Method II, with either high or low volatile cokes, the volatile matter evolved passes out of the small vent between the lid and rim of the crucible and is burned externally; during the test very little of the nonvolatile portion of the coke is consumed, on account of the protection afforded by the tight-fitting lid and the generally nonoxidizing atmosphere maintained in the crucible.

With Method I the amount of volatile matter evolved relative to the air accessible to it is considerably less than in Method II, because of the smaller sample, larger crucible, and loosely fitting lid, all of which make for its quicker dissipation and more readily expose the nonvolatile portion to oxidation, which results in a V. C. M. content considerably above the actual. This is particularly the case with low volatile cokes. As the actual V. C. M. content of the coke tested increases, the combustion of the nonvolatile portion is correspondingly delayed and the results more nearly approach the true value.

Continuous and Intermittent Heating

The high volatile coke was used in comparative tests in which the heats were made both continuous and intermittent for the same total period.

Table VI—Comparison of Loss per cent with Continuous and Intermittent Heats

	7 Min.	14 Min. Continuous	14 Min. Intermittent
10-cc. capsule, 2-g. sample, furnace	3.99	4.22	4.52
20-cc. crucible, 1-g. sample, flame	6.12	8.42	8.51

The test with the 10-cc. capsule shows that the volatile matter is practically all expelled at the end of the 7-min. period. The excessive increase in the 14-min. continuous heat with the 20-cc. crucible must be attributed to the high oxidation factor inherent to this type of apparatus.

It may also be noted that the losses in the intermittent heat tests are somewhat greater than those for the same period of continuous heating, which can be ascribed to the oxidation resulting from air absorbed in the cooling of the intermittent tests. On this basis the correction factor as applied by Method II may be somewhat in excess of the actual, although the result thus corrected is more nearly the value estimated from the continuous and intermittent heats than the uncorrected figure.

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[8] *8th Internat. Congr. Appl. Chem.*, **10**, 139.

V. C. M. uncorrected	4.0 per cent
V. C. M. estimated actual	3.6 per cent (difference on continuous and intermittent subtracted)
V. C. M. by Method II	3.5 per cent

Vanadium Compounds as Driers for Linseed Oil[1]

By F. H. Rhodes[2] and K. S. Chen

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Satisfactory driers for linseed oil may be prepared by heating ammonium metavanadate with rosin or linseed oil. The driers thus prepared, when used in amounts sufficient to give 0.2 per cent of vanadium in the oil, cause it to dry to a hard, tough, smooth film. Vanadium is superior to lead in drying power and gives smoother and tougher films than does manganese or cobalt. The principal objection to the use of vanadium driers is that they darken the oil somewhat.

The initial oxidation of linseed oil containing vanadium drier is much more rapid than that of oil containing an equivalent amount of lead drier, and the rapid absorption of oxygen continues for a much longer time; about 1.75 times as much oxygen is absorbed.

The vanadium driers described in the following paper possess certain advantages not shown by the lead, manganese, or cobalt driers in common use, and should prove very satisfactory in the preparation of certain types of paint and varnish.

THE use of vanadium as a drier for paint oils was suggested by Sabin,[3] who states that "the writer also made a vanadium compound which was a very efficient drier, but of course its cost prevented its use." The cost of the material is not, however, sufficient to prevent the use of vanadium if it were found that such driers were very much more efficient than driers made from the more common metals, or if the discovery of new sources of vanadium or the development of improved processes of recovery from the ore should decrease its cost.

Materials

The linseed oil used in this work was taken from a sample lot of "Superior Grade," pure, raw linseed oil presented to this laboratory by Spencer Kellogg and Sons. The lead, cobalt, and manganese driers which were used for comparison with the vanadium driers were presented by Harshaw, Fuller and Goodwin Company. Upon analysis, these driers were found to contain the following percentages of metal:

Lead linoleate	24.2
Lead resinate (precipitated)	22.5
Manganese linoleate	10.55
Manganese resinate (precipitate)	6.02
Cobalt linoleate	12.25
Cobalt resinate (precipitated)	2.33

Preparation of Vanadium Driers

The pure ammonium metavanadate used in the preparation of the vanadium driers was purchased from the Vanadium Corporation of America.

FROM IGNITED OXIDE—A mixture of 6 g. of vanadium pentoxide, prepared by ignition of ammonium metavanadate, and 100 g. of linseed oil was heated with constant stirring. The mass gradually thickened and became dark green in color. Even after heating to 350° C. for 2.5 hrs., however, a considerable amount of the solid oxide remained suspended in the viscous mass.

In an attempt to prepare the fused resinate from the vanadium pentoxide, 6 g. of the oxide were fused with 100 g. of rosin. Decomposition began at 250° C. and copious fumes were evolved. After 1 hr.'s heating there was obtained a dark green viscous mass which solidified on cooling to a brittle amorphous mass in which particles of unreacted oxide were still visible.

It was thought probable that the failure to obtain complete reaction in these cases was due largely to the fact that the ignited oxide is crystalline and, like many other ignited crystalline oxides, relatively inert. Attempts were made, therefore, to prepare driers by heating together ammonium metavanadate and rosin or linseed oil. Under these conditions the ammonium salt should decompose, evolving ammonia and giving amorphous vanadium oxide which should react readily with the oil or rosin.

FROM AMMONIUM METAVANADATE—Vanadium linoleate was prepared by heating 100 g. of linseed oil to 300° C. and adding 10 g. of ammonium metavanadate slowly and with constant stirring. At each addition of the vanadate, ammonia was evolved and the solid residue reacted readily with the oil. The mixture was heated and stirred for a short time after the addition of the last portion of the ammonium vanadate, and was then allowed to cool. The final product was a dark green waxy mass which showed no particles of unincorporated oxide or vanadate and which contained 3.15 per cent of vanadium by analysis. The rather low vanadium content is due to the fact that considerable "dusting" occurred during the addition of the vanadate.

In the same way, vanadium resinate was prepared by adding 10 g. of ammonium vanadate to 100 g. of rosin at a temperature of 250° C. This resinate was a dark olive-green amorphous solid containing 2.68 per cent of vanadium.

Preparation of Solutions

A series of concentrated drier solutions was prepared by dissolving the linoleates (or resinates) of lead, manganese, cobalt, and vanadium, respectively, in warm linseed oil. In each case the amounts of oil and drier were such as to make 100 g. of drier solution containing exactly 1 g. of the metallic element of the drier. From these solutions four series of solutions of drier in raw linseed oil were prepared, each series consisting of solutions containing, respectively, 0.1, 0.2, and 0.3 per cent of metal. In preparing each solution, the required amounts of raw oil and of concentrated drier solution were mixed and heated to 200° C. in order to secure thorough and uniform incorporation of the drier in the oil.

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[1] Received October 14, 1921.

[2] Professor of Industrial Chemistry.

[3] "Technology of Paint and Varnish," 2nd edition, 38.

COMPARISON OF DRIERS

RELATIVE DRYING TIME—In a series of experiments made to determine the relative drying times of the oils containing the various driers, each sample was painted out in a thin film on a glass plate which was allowed to stand at room temperature until dry. The time required for each sample to "set" (*i. e.*, to dry until no longer sticky when touched lightly with the finger) and to "dry" (*i. e.*, to become hard enough to give no impression when pressed with the finger) was noted. For purposes of comparison, a similar test was made with raw linseed oil containing no drier. The results are shown in Table I.

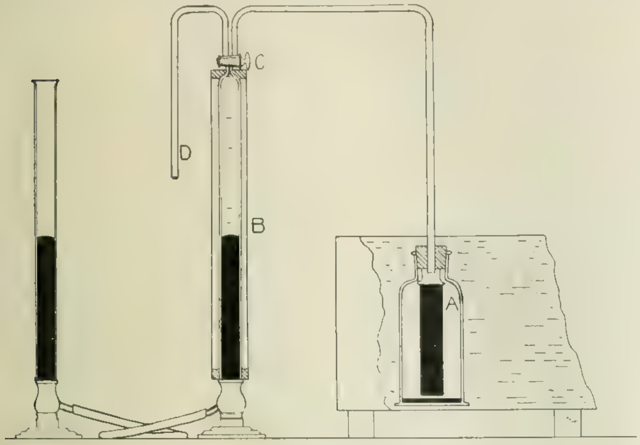

FIG. 1

TABLE I—"SETTING" AND "DRYING" TIMES OF RAW LINSEED OIL WITH VARIOUS DRIERS

DRIER		AMOUNT	Hours to	
Metal	Type	Per cent	"Set"	"Dry"
Manganese	Resinate	0.1	12.5	14
Manganese	Resinate	0.2	15	17
Manganese	Resinate	0.3	17	18
Manganese	Linoleate	0.1	13	13.5
Manganese	Linoleate	0.2	15	17
Manganese	Linoleate	0.3	17	17
Cobalt	Resinate	0.1	4.5	5.5
Cobalt	Resinate	0.2	4.5	6
Cobalt	Resinate	0.3	5.5	8
Cobalt	Linoleate	0.1	5	6.5
Cobalt	Linoleate	0.2	4.5	6.5
Cobalt	Linoleate	0.3	4	5.5
Vanadium	Resinate	0.1	7	9
Vanadium	Resinate	0.2	6	8
Vanadium	Resinate	0.3	6	8.5
Vanadium	Linoleate	0.1	7	9.5
Vanadium	Linoleate	0.2	6	8.5
Vanadium	Linoleate	0.3	6	8.5
Lead	Resinate	0.1	38	42
Lead	Resinate	0.2	29	32
Lead	Resinate	0.3	28	31
Lead	Linoleate	0.1	38	42
Lead	Linoleate	0.2	29	32
Lead	Linoleate	0.3	27.5	31
Raw linseed oil	....	...	57	63

It will be observed that an increase in the concentration of manganese drier, either resinate or linoleate, causes an increase in both the setting time and the drying time. This is due to the fact that with the higher concentrations of manganese the oil film "casehardens," *i. e.*, a tough film forms rapidly at the surface and, by excluding the air from the lower part of the film, actually increases the drying time.

The results in Table I indicate that vanadium driers are much more efficient than lead or manganese driers. Oils containing vanadium driers dry about twice as rapidly as do oils containing an equivalent amount of manganese drier, and almost five times as rapidly as do oils containing an equivalent amount of lead drier. Vanadium driers are only slightly less efficient than cobalt driers.

CHARACTER OF FILM—Like cobalt, vanadium appears to cause the oil to dry uniformly throughout its mass. No tendency to the formation of surface films or "skins" was observed.

The films with manganese drier showed a distinctly wrinkled appearance after drying. Cobalt also caused some wrinkling. The oils made up with the lead or vanadium drier gave perfectly smooth films.

Each film was allowed to stand for 1 wk. after it was classed as "dry," and was then examined for toughness by scratching with the point of a knife. The films containing manganese were distinctly brittle, and broke away in small scales. Those made with cobalt drier were somewhat brittle, and broke in short strips from the edge of the knife. Films containing lead or vanadium were tough, coming away in long curling ribbons.

The oils containing vanadium driers were darker in color than the others, and gave brownish films. It is possible that this darkening might be decreased or eliminated by varying the procedure used in preparing the drier. In any case, the color would be objectionable only in the preparation of white paints or specially pale varnishes.

COMPARISON OF VANADIUM AND LEAD DRIERS

In order to obtain a more quantitative comparison of the drying properties of vanadium and of lead, a series of experiments was made to determine the effect of the respective driers upon the rate of absorption of oxygen by linseed oil.

The apparatus is shown in Fig. 1. The wide-mouthed bottle A was immersed in a thermostat, the temperature of which was constant to within 0.1° C. The bottle was closed by a tightly fitting rubber stopper, through which was inserted a glass tube connected to one outlet of a mercury-filled Hempel gas buret, B. The other outlet of the buret was connected, by tube D, with a tank of oxygen. Two duplicate pieces of apparatus were constructed, so that parallel tests on the two driers could be made at the same time and under as nearly as possible identical conditions.

PROCEDURE—A strip of cotton filter cloth, 10 in. long and 1 in. wide, was weighed, saturated with oil containing the desired amount of drier, and again weighed to determine the weight of the sample. One end of the strip was attached to a copper wire in such a manner that the cloth hung flat and free from folds, and wire and cloth were suspended in the bottle as shown. Before placing the sample in position the bottle was filled with oxygen at atmospheric pressure, and a small amount of concentrated sulfuric acid was placed in the bottom of the bottle to absorb any water vapor that might be formed during the oxidation of the oil. The stopper carrying the inlet tube and the wire from which the sample was suspended, was then inserted tightly. Exactly 100 cc. of dry oxygen at known (atmospheric) pressure and known temperature were drawn into the buret, the stopcock was so turned as to connect the buret with the bottle, and the apparatus was allowed to stand in this position. As the

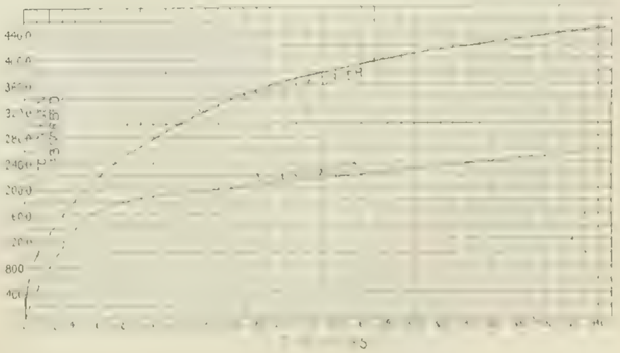

FIG. 2

TABLE II—OXYGEN ABSORBED BY LINSEED OIL WITH LEAD AND VANADIUM DRIERS

TIME Hrs.	Cc. Oxygen Absorbed Calc. to 0° C., 760 Mm. Hg Vanadium	Lead
1.5	50.1	4.17
3.5	70.4	12.9
5	81.8	24.4
6.5	91	29.9
9	97	43.5
11.4	112.4	51.1
23	141.5	93.8
27.5	154	104
30.5	157	116.6
33.5	162.5	121.5
35.5	170.5	128.1
46.5	205	155.8
54.5	221.3	159
73	240	169.5
81	251.5	174.7
94.5	272	183.5
104.5	285	191.6
128.5	311.2	196.2
153.5	333.4	203
179	348	208.7
203	363.9	214.5
247	383	219.8
286	406.5	232
382	435	247
430	444	252

oxygen was absorbed by the oil, the leveling tube of the buret was raised so as to maintain atmospheric pressure within the apparatus. At definite intervals readings were taken to determine the amount of oxygen absorbed by the oil. The experiment was continued until the rate of absorption of oxygen became very slow.

Duplicate runs were made with samples of linseed oil containing lead drier and vanadium drier, respectively. The temperature of the thermostat was kept constant at 30° C. ± 0.1° C. The amount of drier in each sample was equivalent to 0.2 g. of metal (lead or vanadium) in 100 g. of the sample. The weight of the sample of oil containing the lead drier was 1.0224 g., while the sample made up with vanadium drier weighed 1.0403 g.

The results obtained in these experiments are shown in Table II.

These results are shown graphically in Fig. 2. It will be observed that in the case of the oil containing the lead drier, the absorption of oxygen proceeded rather rapidly for about the first 80 hrs., and continued rather slowly and uniformly until the end of the run. The rate of oxidation of the sample containing vanadium drier was very high during the first 10 hrs., decreasing slowly and continuously throughout the remainder of the experiment.

It is of interest to note that the oil containing vanadium drier absorbed, during the period of observation, a total amount of oxygen equivalent to 1.76 times the amount of oxygen absorbed by the sample prepared with lead drier.

The Soil Solution[1]

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THE investigator of "alkali soils" often has difficulty in obtaining a clear filtrate because in the watery extract the degree of dispersion of the colloidal disperse phase is so great and in such a stable form that the solution may be kept for years[1,*] without flocculation. The particles of such a phase are so small that it is impossible to separate them by ordinary filtration. It is imperative, however, that the soil extract be free from colloidal particles; colored colloids interfere with sharpness of end reaction in colorimetric and some volumetric reactions, and where the colloid is of a proteinous nature, subsequent reduction may liberate nitrogen or ammonia which in the end reaction may be interpreted as nitric nitrogen. Furthermore, the colloids may actually combine with one or more of the reagents giving erroneous results. The ideal method of obtaining a clear, aqueous solution would be one which yielded a clear solution without filtration. This would necessitate the addition of a flocculent to the soil infusion. Such a substance should be rapid in action and should remove only a minimum quantity of the soluble salts from the solution, and must not interfere with the sensitiveness of the method.

The work of Linder and Picton[2] on flocculents is especially valuable, as they tested the precipitating powers of various salts on arsenious sulfide solution. Aluminium sulfate was the most efficient compound used, followed by aluminium chloride. Ferric sulfate was only about one-third and calcium salts only about one-fourth as effective; 3200 times as much sodium chloride as aluminium sulfate were required to produce the same effect. McGeorge[3] found aluminium sulfate the most efficient flocculent for clay. Wolkoff[4] found the aluminium compounds among the best flocculents, but there was a great variation, depending upon the soil. This is to be expected from Hardy's rule that the precipitating power of an electrolyte for a colloid depends on the valence of the ion which carries the electric charge opposite that of the dispersoid. The colloids found in the soil may be either the electronegative colloid—clay—or the positive or negative organic colloid.

Buhlert and Fickenday[5] recommended the addition of 2 per cent of sodium chloride, whereas King and Whitson[6] used potassium alum. The quantity of alum recommended, however, gave with some soils[7] a cloudy solution which had to be filtered before it could be compared in the colorimeter. Furthermore, in the presence of sulfates there is a loss of nitrates when the phenoldisulfonic acid method is used. Chamot[8] and co-workers found aluminium cream the best precipitating agent of several tested for organic matter, and that it occasioned no loss of nitrates. Lipman and Sharp[9] found potassium alum, aluminium cream, and boneblack all decidedly unreliable, inducing losses of nitrates in the phenoldisulfonic acid method. They found lime to be much more reliable, but it must not be used with chloroform because the double decomposition which takes place produces chlorides, which interfere with the accurate determination of nitrates.[10] One of us has used the Pasteur-Chamberland filter very extensively in his work[11] on soil nitrates. This gives a clear solution and occasions only slight losses of nitrates.[12]

COMPARISON OF CLARIFYING AGENTS

Sodium, potassium, and iron alum, ferric sulfate, lime, finely precipitated calcium carbonate, and talc, together with the centrifuge and the Pasteur-Chamberland filter, were tested on a number of soils rich in soluble salts and having a high clay or organic colloidal content. These agents could be arranged in a descending order of efficiency as follows: Pasteur-Chamberland filter, ferric alum, ferric sulfate, sodium alum, potassium alum, centrifuge, talc, calcium carbonate.

The centrifuge was run at a speed of 1200 r. p. m., and some solutions were not clear after 30 min. centrifuging. Many soil-water mixtures to which talc or calcium carbonate were added were not clear after several hours.

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[2] Chemist, Utah Agricultural Experiment Station.

[3] Associate Chemist.

[*] Numbers in text refer to Bibliography at end of paper.

The quantity of the specific salt recovered varied, depending upon the method used in clarifying the solution (Table I).

TABLE I—PERCENTAGES OF NITRATES, CHLORIDES, AND SULFATES RECOVERED FROM CLARIFIED SOLUTIONS

	Salt Recovered				
Method	Nitrates Per cent	Chloride Per cent	Sulfates Per cent	Method	Nitrates Recovered Per cent
Filter	98.4	100.1	100.1	Ferric sulfate	96.5
Centrifuge	97.0	...	...	Calcium oxide	96.5
Sodium alum	99.2	100.0	...	Calcium carbonate	96.3
Potassium alum	99.6	...	...	Talc	94.6
Ferric alum	93.7	...	...	....	..

Since neither calcium carbonate nor talc gave clear solutions, they can be discarded. Conclusive evidence has been produced to show that when lime is used in the determination of nitric nitrogen by the phenoldisulfonic acid, the aluminium reduction,[13] or the Ulsch reduction methods,[14] low results are obtained. This is not due to the lime carrying out with the colloid some of the nitrate, for similar results are obtained when lime is added to a pure solution of sodium nitrate and the nitric nitrogen determined directly by the Ulsch method.

It therefore appears that the Pasteur-Chamberland filter, centrifuge, or sodium or potassium alum is best suited to use as a flocculent in the determination of nitric nitrogen in the soil. Moreover, the evidence is conclusive that the filter does not retain quantities of chlorides, sulfates, or nitrates sufficient to vitiate the results in soil analysis.[14] Only the filter or centrifuge can be used where sulfates are to be determined in the solution.

Five grams of alum may be added to a soil solution without its interfering with the recovery of nitrates or sulfates, but the writers have yet to find a soil which requires over 2 per cent to give clear filtrates. On the other hand, when lime is used as the flocculent the quantity of nitric nitrogen recovered is inversely proportional to the quantity of lime added to a soil-water mixture.

TIME OF EXTRACTION

The time necessary for water to dissolve the salts within a soil may vary greatly with the condition of the soil when the water is added, as well as the treatment given the mixture. If the water is not left in contact with the soil for a sufficient length of time some of the salts may be left unextracted, and if left too long denitrification may take place. Yet we find a large variation in the time recommended by different workers.[5,6,11,15,16,17]

In order to obtain more exact information on this subject, the writers extracted with 500 cc. of water for varying lengths of time 100-g. portions of various soils containing, in the case of nitrates and chlorides, 2 g. of alum. When sulfate was determined the alum was omitted. The samples, in 1000-cc. bottles, were agitated in a mechanical shaker for the time indicated and allowed to stand long enough to settle (not over 10 min.), and the nitrates, chlorides, and sulfates were determined by the Ulsch,[14] Volhard,[18] and gravimetric methods,[19] respectively. The average results for a number of determinations are given in Table II.

TABLE II—PERCENTAGES OF NITRATES, CHLORIDES, AND SULFATES EXTRACTED FROM SOIL IN VARYING LENGTHS OF TIME

	Time of Shaking (Minutes)							
SALT	5	10	15	20	30	35	40	45
Nitric nitrogen	100.4	100.4	98.5	...	101.3	101.3	98.1	...
Chlorides	100.1	100.3	..	100.0	100.2	..	..	99.9
Sulfates	88.3	...	..	100.8	97.6	...	102.8	101.7

Inasmuch as these tests were made on finely powdered soil and the soil-water mixture was thoroughly agitated for the time indicated, they would not represent the condition where unpulverized soil was treated with water. So far as the nitrates and chlorides are concerned nothing is to be gained by shaking the soil longer than 5 min., but in the case of the sulfates equilibrium is not reached until they have been shaken 40 min.

These results were obtained from solutions not nearly saturated. For example, at 0° 100 g. of water will dissolve 26.9 g. of anhydrous magnesium sulfate, or 76.9 g. of the heptahydrate, or 4.8 and 55.59 g. of the corresponding salts of sodium. Under the present conditions there are present but 2.25 per cent of sulfates calculated as sulfuric acid (about half and half sodium and magnesium sulfates). If, as frequently happens, soils are rich in gypsum, much longer shaking will be necessary to attain equilibrium in any ratio of soil to water which we wish to use.

RATIO OF SOIL TO WATER

We find little regularity in the ratio of water to soil, used by different workers.[5,6,15,20,21,22] In the present investigation, the writers have made determinations of the various salts in soil and soil to which dried blood was added, varying only the ratio of water to soil. The average results for a number of determinations are given in Table III.

TABLE III—PERCENTAGES OF SALTS EXTRACTED WITH VARYING RATIO OF SOIL TO WATER

	RATIO				
SALT	1:5	1:10	1:15	1:20	1:25
Nitric nitrogen	99.8	98.6	97.2	97.8	100.0
Sodium chloride	99.9	100.0	99.5	99.9	...
Sulfates	99.6	98.8	101.2	100.0	...

The difference found is only what could be attributed to experimental error. Hence, we may conclude that the ratio of soil to water is immaterial, provided the soil does not contain sufficient salt to give a saturated solution. However, the water in the sample must be taken into consideration. The facts that the same quantity of salt is extracted with the varying quantities of water and that nearly 100 per cent is recovered in the various experiments reported in this work make it very doubtful if Allen and Bonazzi's[23] contentions are justified, that the determination of the nitric nitrogen in the water extract does not give a determination of the nitric nitrogen in the soil.

USE OF AN ANTISEPTIC

Most workers assume that if the soil is to stand in contact with the water any length of time and nitrates are to be determined, an antiseptic should be added; yet, we have no definite information as to its quantity. In many cases the quantity added may actually accelerate the biological transformations going on in the soil. Moreover, it is not immaterial what antiseptic be used, for chloroform[10] used in the presence of lime with the phenoldisulfonic acid method gives inconsistent results.

In order to determine the error due to the standing of the soil solution, 100-g. portions of a rich garden soil were treated with water and varying quantities of nitric nitrogen and the quantity of nitric nitrogen present was determined after varying lengths of time. The average results are given in Table IV.

TABLE IV—MILLIGRAMS OF NITRIC NITROGEN RECOVERED FROM SOIL AFTER VARYING LENGTHS OF TIME

	Nitrogen Recovered in		
Hours	100 G. Soil	100 G. Soil + 20 Mg. N. N.	100 G. Soil + 40 Mg. N. N.
0	36.85	53.35	72.85
24	36.53	53.44	72.23
48	34.00	55.28	70.00
120	26.00	50.40	67.20
144	19.90	46.24	53.95

After the first 24 hrs. there was a gradual increase in loss. This indicates that the loss where the solutions are to stand some time may be appreciable. However, considerable quantities of nitric nitrogen disappear from a mixture of soil and fresh horse manure. This is often considerable during the first 24 hrs., even in the presence of 2 per cent of sodium alum. Repeated tests of water extracts of ordinary fertile soils kept at 24° C. for 24 hrs. showed no loss of nitric nitrogen, and even after 48 hrs. the loss was always very small.

It is evident, therefore, that where the soil-water mixture, or the soil extract, is to stand some time precautions must be taken to prevent a loss of nitrogen. The antiseptics which have been used are lime, alum, chloroform, and thymol. Lime interferes with the determination of nitric nitrogen and can be discarded. The results from tests on the other three are given in Table V.

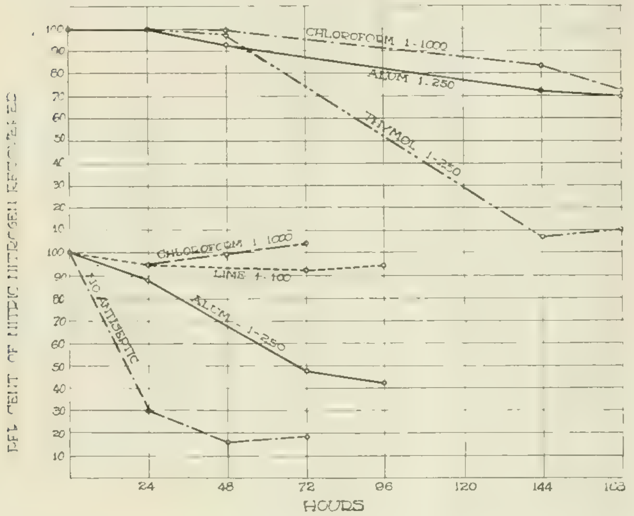

Fig. 1

Table V—Milligrams of Nitric Nitrogen in Soil after Varying Lengths of Time with Antiseptic

Treatment	At First	After 24 Hrs.	After 48 Hrs.	After 144 Hrs.	After 168 Hrs.
Soil + 2 g. alum	48.00	47.63	45.20	35.00	33.60
Soil + 2 g. alum + 20 mg. nitric nitrogen	67.96	67.26	65.44	58.14	55.34
Soil + 2 g. alum + 40 mg. nitric nitrogen	89.68	87.28	84.34	77.01	72.85
Soil + 2 g. alum + thymol	49.04	49.00	48.30	4.00	5.00
Soil + 2 g. alum + thymol + 20 mg. nitric nitrogen	69.36	67.68	67.96	4.40	4.00
Soil + 2 g. alum + thymol + 40 mg. nitric nitrogen	89.26	88.36	8.26	1.40	4.00
Soil + chloroform	51.80	51.80	51.30	43.40	37.80
Soil + chloroform + 20 mg. nitric nitrogen	71.94	71.87	71.46	60.66	57.55
Soil + chloroform + 40 mg. nitric nitrogen	88.46	91.06	88.26	80.84	72.86

Similar data are illustrated graphically in Fig. 1, in which the upper graphs give results obtained on a rich greenhouse soil, while those at the bottom are from a soil-manure mixture.

Table VI—Milligrams of Nitric Nitrogen from Soil and Manure after Varying Lengths of Time

Treatment	Nitric Nitrogen Found			
	At First	After 24 Hrs.	After 48 Hrs.	After 72 Hrs.
Soil, no antiseptic	3.064	0.826	0.49	0.56
Soil + 2 g. alum	3.117	2.732	2.59	1.96
Soil + 2 g. alum + 0.5 cc. $CHCl_3$	3.067	2.980	3.06	3.22
Soil + 2 g. alum + 1.0 cc. $CHCl_3$	2.956	2.840	2.90	2.91
Soil + 2 g. alum + 2.0 cc. $CHCl_3$	2.800	3.010	2.90	2.89
Soil + 2 g. alum + 3.0 cc. $CHCl_3$	2.790	2.910	2.93	3.16

It is evident from the results reported in Table VI that nothing is to be gained by adding over 0.5 cc. of chloroform to 100 cc. of the soil-water mixture. Moreover, as these results clearly show, more concordant results are obtained when analyses are made immediately and the authors dispense with an antiseptic.

The losses of nitrogen reported in most of this work are maxima and probably would never be duplicated in regular work, because the soil contained such large quantities of nitrates and fresh horse manure. Moreover, the solutions were kept in an incubator at 24° C. during various intervals. It would appear that under ordinary conditions, where the time in which the soil is in the water is short and the temperature comparatively low, no loss would result with ordinary soil where the 2 g. of alum had been added.

Summary

Clear soil extracts may be obtained by adding 2 g. of lime, ferric sulfate, ferric alum, sodium alum, or potassium alum to the soil-water mixture, by filtering through the Pasteur-Chamberland filter, or by centrifuging. The last three procedures give a clear solution with a minimum loss of salt. Lime, ferric sulfate, and ferric alum cause a considerable loss of nitrates.

In the determination of chlorides and nitrates nothing is to be gained by agitating the soil and water for more than 5 min., provided the soil is finely divided and the solution vigorously shaken. A longer time of agitation is required to reach equilibrium in a soil solution in which sulfates are to be determined. This time will depend upon the quantity and quality of sulfates present.

Usually a ratio of one part of soil to five of water is sufficiently wide, but this also will depend upon the quantity and kind of sulfates present.

Where nitrates are to be determined in the soil solution and alum is used as the flocculent, no other antiseptic is necessary; where alum is not used and the solutions are to stand for some time it is well to add 0.5 cc. of chloroform to each sample.

Bibliography

1—W. H. Brewer, "Suspension and Sedimentation of Clays," *Am. J. Sci.*, **29** [3] (1885), 1.

2—S. E. Linder and H. Picton, "Solution and Pseudo-solution. II—Some Physical Properties of Arsenious Sulfide and Other Solutions," *J. Chem. Soc.*, **67** (1895), 63.

3—W. McGeorge, "Effect of Fertilizers on Physical Properties of Hawaiian Soils," Hawaii Agr. Expt. Sta., *Bull.* **38** (1915).

4—M. I. Wolkoff, "Studies on Soil Colloids," *Soil Science*, **1** (1916), 585.

5—Buhlert and Fickenday, "Determination of Nitric Acid in Soils," *Landw. Vers. Sta.*, **63** (1906), 239.

6—F. H. King and A. R. Whitson, "Development and Distribution of Nitrates and Other Soluble Salts in Cultivated Soils," Wisconsin Agr. Expt. Sta., *Bull.* **85** (1901), 38.

7—R. Stewart and J. E. Greaves, "Study of Production and Movement of Nitric Nitrogen in an Irrigated Soil," Utah Agr. Expt. Sta., *Bull.* **106** (1909), 80.

8—E. M. Chamot, D. S. Pratt and H. W. Redfield, "Study of Phenoldisulfonic Acid Method for Determination of Nitrates in Water," *J. Am. Chem. Soc.*, **33** (1911), 366.

9—C. B. Lipman and L. T. Sharp, "Studies on Phenoldisulfonic Acid Method for Determining Nitrates in Soils," Univ. of Cal., *Pub. Agr. Sci.*, **1** (1912), No. 2, 21.

10—R. Stewart and J. E. Greaves, "Influence of Chlorine on Determination of Nitrates by Phenoldisulfonic Acid Method," *J. Am. Chem. Soc.*, **35** (1913), 579.

11—R. Stewart and J. E. Greaves, "Production and Movement of Nitric Nitrogen in Soils," *Centr. Bakt. Parasitenk.*, *Abt. II*, **34** (1912), 119.

12—Lyman J. Briggs and Macy H. Lapham, "Capillary Studies and Filtration of Clay from Soil Solutions," Bur. Soils, *Bull.* **19** (1902), 31.

13—R. S. Potter and R. S. Snyder, "Determination of Nitrates in Soil," This Journal, **7** (1915), 863.

14—J. E. Greaves and C. T. Hirst, "Some Factors Influencing Quantitative Determination of Nitric Nitrogen in Soil," *Soil Science*, **4** (1917), 179.

15—E. Gutzeit, "Determination of Nitric Acid in Soils," *Landw. Vers. Sta.*, **65** (1906), Nos. 3 and 4, 217.

16—Webel, Frankfurt and Duschetschkin, "Method of Determining Nitric Acid in Soils," *Vyestnik Sakh. Prom.*, **44** (1906), 652; abstr., *Expt. Sta. Record*, **19** (1906), 110.

17—V. I. Sasanov, "Determination of Nitric Acid in Chernozem Soils," *Zhur. Opuit. n. Agron.* (*J. Russ. Expt. Landw.*), **7** (1906), 381; abstr., *Expt. Sta. Record*, **19** (1906), 110.

18—C. T. Hirst and J. E. Greaves, Unpublished Results.

19—C. T. Hirst and J. E. Greaves, Unpublished Results.

20—E. Fricke, "Quantitative Determination of Nitric Nitrogen," *Z. angew. Chem.*, **5** (1891), 239.

21—T. F. Schmidt, "Determination of Nitrogen in Nitrate and Nitrate Mixtures by Reduction of Nitric Acid," *Chem.-Ztg.*, **17** (1893), 173.

22—J. Litzendorff, "Use of Nitron for Determination of Nitric Acid in Soils and Plants," *Z. angew. Chem.*, **20** (1907), 2209.

23—E. R. Allen and A. Bonazzi, "On Nitrification," Ohio Agr. Expt. Sta., *Tech. Bull.* **7** (1915).

Composition Basis for Considering Water Requirements of Plants[1,2]

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The results of field and greenhouse experiments recorded in the following paper indicate that fertilization of a soil which responds to direct or indirect fertilizer treatment allows the plants to make their growth on a smaller amount of water and to have a different composition from what they otherwise would.

The same effect is produced by cultivation, which by opening up the soil increases bacterial activity, which in turn gives increased concentration of the soil solution.

Proper fertilization and cultivation minimize dangers to crops from drought injury in humid regions of the United States by having the plant go into the drought period with an accumulative reserve of soil moisture.

This work opens up the study of fertilization from the basis of water requirement.

There is hardly a plant for which one cannot find wide ranges in the published analyses. Different experiment stations have tried to produce high protein corn or to raise the content of some valued constituent in another crop. This question of variation in analysis is so mixed up with food chemistry that the writer has thought it worth while to search for reasons for this variation.

Some investigators have analyzed plants to find out what fertilizer constituents they contain, and have attributed the variations in analysis to lack of fertilizer constituents in the soil. In accordance with Liebig's theories, they have added plant food to the soil in quantities equal to those taken out by the crop. Another method of study of plant growth has been to try to determine directly from the soil analysis what is lacking, and how to fertilize for increased crops. The writer has worked out a rather novel method of attacking the problem, namely, the application of different fertilizer materials to the soil, and a study of the variation in plant composition and water requirements caused by these fertilizer treatments.

Field Experiments

In some experiments made in 1914 in orchards where cultivation was the largest variable, the writer found large differences in the moisture content of the soil at only one period of the year. The data in Table I show conditions in this young orchard. The results show that differences in soil management gave entirely different trees, as indicated by circumference gains, average weight of leaf, and per cent nitrogen in leaves. The importance of cultivation, by which air is let down into the soil and chemical reactions allowed to take place, is clearly shown in this table.

The two plots where the trees made the greater growth have much larger nitrate contents and have lost relatively much less water up to the height of the growing season. Records on rainfall have been kept, and study of the relative absorption and retention of water by this soil under the different systems of management has shown very little difference under the cultural treatments in the absorptive capacities of the surface with prevailing rates of rainfall. It appears, then, that the immense differences in the changes of relative weights of water in the soil must have something to do with the water utilization by the plants.

Kiesselbach of Nebraska makes the following statement:[3] "Up to an optimum soil productivity the amount of water transpired per pound of dry matter reduces with an increase in available nutrients." Again he says:[4]

> 21—The water requirement per pound of dry matter is much larger in an infertile soil than in a fertile soil. Increasing the fertility of the soil reduces the water requirement for grain production and for total dry matter. An application of manure has a much greater effect upon an infertile than upon a fertile soil. Thus, as an average for 2 yrs., equal applications of sheep manure to infertile, intermediate, and fertile soils reduced the water requirements for ear corn production 42.6, 25.4, and 10.5 per cent, respectively. For total dry matter these water requirements were reduced 28.9, 17.1, and 8.1 per cent, respectively. However, the total water requirement per plant was increased by an application of manure to infertile, intermediate, and fertile soil, respectively, 106.7, 42.6, and 28.7 per cent. From these figures it is apparent that increasing the fertility does not reduce but rather greatly increases the total amount of water necessary per plant. This is due to increased plant growth. The reduction in water requirement per pound of dry matter is due, not to some effect of a denser soil solution upon the need for a rapid transpiration rate, but, rather, simply to a more thrifty and vigorous growth of the plant, resulting from a more favorable supply of food materials. It appears to be more a matter of nutrition than of transpiration.
>
> 23—The average water requirement per pound of dry matter of two varieties of corn which had been grown for many years under the humid conditions of New York was approximately the same as the average for two varieties which had been grown continuously under the relatively dry conditions of western Nebraska.

Table I—Orchard Management Investigations

(Data under Different Systems of Soil Management)

	Clean Culture Cover Crop	Accumulative Straw Mulch	Sod for Several Years
Average circumference gains of trees 1911–1916, cm.	25.5	25.9	17.1
Average weight per leaf, grams	1.18	1.49	1.08
Nitrogen in leaves, per cent	2.31	2.36	1.71
Average nitrate content of soil during growing season	57.5[1]	47.0[1]	14.5[1]
Relative wts. water in soil at start of growing season, lbs.	11.40[2]	11.56[2]	11.86[2]
Relative wts. of water in soil at height of growing season, lbs.	8.45[2]	11.27[2]	3.78[2]
Change in relative wts. of water in soil, lbs.	2.95[2]	0.29[2]	8.08[2]

[1] Parts NO_3 per million parts of dry soil.

[2] Areas of surface 12 in. by 12 in. by 9 in. in depth.

Kiesselbach's field work was largely under relatively dry conditions throughout the growing season. It is the writer's observation that in most of the humid regions of the United States periods of water deficiency are relatively short; therefore the decrease in relative water requirements of variously fertilized plants will let those under better conditions go through the drought on an *accumulative water reserve*. Moisture determinations made for several years in the orchard reported on in Table I show that variations in moisture were not accounted for by relative differences in the water absorbing and evaporating powers of the soils of the different plots. Ample water was always present during drought periods on those plots where increased fertility was shown by leaf weight, nitrogen content of leaves, and relatively higher growth characteristics.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] The basis for this work consists largely of data secured by the author or under his direction while in the employ of Purdue University Agricultural Experiment Station.

[3] Letter to the author.

[4] Nebraska Agr. Expt. Sta., *Research Bulletin* **6**, 15.

On the basis of these facts and certain other observations, the writer considered that soils of humid regions contain ample moisture, under all systems of treatment, at the start of the growing season. The moisture differences at the height of the season were so large when different plots were compared (during so-called drought periods) that the conclusions drawn in the introductory paragraphs seem tenable.

GREENHOUSE EXPERIMENTS

Greenhouse experiments were organized on the basis of this field work, according to most careful and approved methods, with variations in fertilization, to see if the use of water by plants bears any direct relation to plant composition. The moisture content of the soil was kept uniform in all cases and the cultural pots were so rotated that differences of light and other factors of the greenhouse would be overcome.[5]

TABLE II—VARIATIONS IN WATER REQUIREMENTS AND PLANT COMPOSITION DUE TO DIFFERENT FERTILIZER TREATMENTS OF *Capsicum Annuum Abbreviatum*

	Check[1]	One Application of Limestone	Two Applications of Limestone	Three Applications of Limestone and Phosphorus Fert.	Three Applications of Limestone and Nitrogen Fert.
Water requirement per unit dry matter	1785	1415	1402	1323	1215
Height of plants at maturity, cm.	25.3	24.2	26.9	29.4	34.5
Wt. of peppers harvested, grams	160	182	212	258	418
Dry weight of four plants, grams	43.1	42.7	43.8	51.8	80.5
Nitrogen in plants, per cent	1.33	1.30	1.30	1.32	1.53
Ash of plants, per cent	7.12	7.00	7.08	6.53	5.79

[1] Soil was Sioux silt loam taken from the experimental field at the Indiana Agricultural Experiment Station.

Table II shows a decrease in water requirement due to fertilization, which varies inversely as the weight of peppers produced and as the dry weight of the plants themselves. The per cent of nitrogen in the plants bears an inverse relation to the water requirement and a direct relation to the per cent ash. These experiments are taken as proof that the water requirement of a plant is decreased by fertilization when the plant is grown on a soil which responds to fertilization.

TABLE III—VARIATION IN WATER REQUIREMENTS AND PLANT COMPOSITION DUE TO DIFFERENT FERTILIZER TREATMENTS OF HEAD LETTUCE

	Check[1]	5 Ton Dry Manure[2]	NPK[3]	10 Ton Dry Manure	Double NPK	5 Ton Dry Manure and NPK
Water requirement per plant as harvested	37.9	24.3	21.9	22.3	16.0	16.1
Green weight, grams	20.7	34.1	66.4	57.5	115.5	80.3
Moisture content of plants, per cent	87.9	89.8	92.1	91.8	92.3	93.1
Nitrogen in tops of plants, per cent	1.48	1.75	2.21	2.08	2.44	2.58
Nitrogen in roots of plants, per cent	0.87	0.84	0.93	0.81	0.96	1.07
Phosphorus in ash of plants (tops), per cent	0.25	0.36	0.40	0.36	0.67	0.69
Calcium in ash of plants (tops), per cent	1.84	2.74	3.06	1.96	2.81	2.08

[1] An open sandy soil was used.

[2] Well rotted horse manure containing 65 per cent moisture used.

[3] NPK from dried blood, banner bone, and muriate of potash in quantities of each element equal to one-third the nitrogen in 5-ton dry manure.

The data given in Table III are confirmatory of those presented in Table II, although obtained on a different soil and with a different plant.

Table III shows that:

1—The 5-ton manure with complete fertilizer has decreased the units of water required to produce one part of green weight by over one-half.

2—The weight of plants grown show a variation of nearly 400 per cent based on the check.

3—The changes in water requirement through a study of moisture content of the plants, the per cent nitrogen in tops, the per cent nitrogen in roots, the phosphorus content of plant ash, and the calcium content of plant ash are evidence that plant composition and water requirement bear a relation.

This work shows the fallacy of the old statement that "fertilization burns out the soil."

There is a common saying, "Cultivate to conserve soil moisture and you will have larger crops." The author believes that "cultivate to let air into the soil, thereby increasing bacterial activities which in turn cause the plants to get more plant food and grow larger on less moisture," would be nearer the truth.

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[5] *Botan. Gaz.*, **66** (1918), 364.

Eastman Pure Organic Chemicals

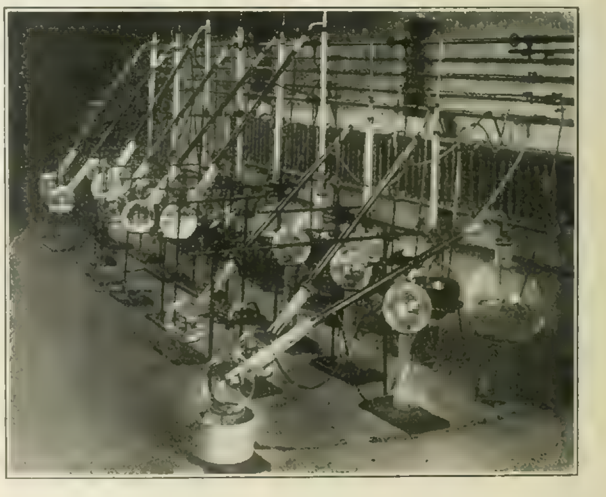
The lecture by C. E. K. Mees and H. T. Clarke on "The Preparation of Synthetic Organic Chemicals at Rochester," which was delivered at the Montreal Meeting of the Society of Chemical Industry last August, is being distributed in pamphlet form by the Eastman Kodak Company.

After discussing the war crisis which necessitated the manufacture in this country of pure chemicals for use in research, the authors describe in interesting detail the laboratories of the Eastman Company which are devoted to this work.

Laboratories and equipment differ in many respects from the research laboratory and from the industrial laboratory. On account of the large number of products required in small amounts, it is not feasible to instal large-scale apparatus suitable for one process only. On the other hand, operating on the laboratory scale is very expensive. The problem is, therefore, to operate with apparatus applicable to as many processes as possible, and to work on as large a scale as this limitation permits.

As an example of the modifications, the cement floors are bounded by open gutters, while supply pipes for water, gas, compressed air, vacuum, steam, and electricity run along the walls. A great deal of work can thus be carried out on the floors, with economy of space and other advantages. The accompanying photograph illustrates such a set-up for fractional distillation.

The pamphlet is abundantly illustrated with photographs of modified laboratory equipment.



At the end of the first six months of work only 265 chemicals were listed for sale. At the present time, 1144 chemicals are listed, of which 700 have been prepared or purified in this laboratory.

The Physiological Principles Governing Ventilation When the Air Is Contaminated with Carbon Monoxide[1,2]

By Yandell Henderson and Howard W. Haggard

Laboratory of Applied Physiology, Yale University, New Haven, Conn.

VITIATION of the atmosphere by the products of combustion and especially of incomplete combustion is recognized as one of the most important industrial conditions affecting health. Progress in this field has, however, dealt chiefly with the effects of high concentration of the gases concerned; that is, with conditions verging on asphyxia. Thus the investigations carried out heretofore for the United States Bureau of Mines have had chiefly in view estimations of such conditions as the amount of exhaust gas from traction engines which would be distinctly dangerous to coal miners, and the concentration of carbon monoxide which, after an explosion, would incapacitate the men from escaping. But in regard to the effects of small amounts of carbon monoxide and related gases, and the dependence of these effects, especially decrease of mental and physical efficiency, upon duration of exposure, there have not been collected data upon which definite standards could be based.

The plan to construct tunnels under the Hudson River between New York and Jersey City for the use principally of motor vehicles has therefore raised several problems which have previously never been extensively investigated. Whereas the conditions in coal mines and about gas producer plants apply only to healthy men, the conditions which will prevail in the tunnel under the Hudson River will affect the general public, not only healthy adults but children and even invalids. The amount of traffic is likely to be large, even from the beginning, and is likely to increase in a few years to the maximum capacity of the roadway. The total amount of exhaust gas discharged from passenger cars and trucks will therefore be considerable. The distance between the ventilating shafts at the pier heads on the two sides of the river will be somewhat more than 3300 feet—a distance greater than in any existing tunnel used by motor vehicles—and the total length of the tunnel about 8500 feet between portals. The ventilation must, therefore, be ample to prevent not only danger, but even slight discomfort, and must be managed in such a fashion as to avoid excessive wind velocities. The cost of installing ventilating fans will, in any case, be an appreciable item in the initial construction, and the maintenance of artificial ventilation during the operation of the tunnel is likely to be one of the largest single items of continuing expense.

Accordingly, the commissions of the states of New York and New Jersey through their Chief Engineer, Mr. Clifford M. Holland, contracted with the Bureau of Mines to undertake on their behalf the investigation of these basic problems:

1—The amount and character of the exhaust gas produced by various types and sizes of passenger cars and trucks.

2—The nature of the toxic substances in exhaust gas, and their allowable concentration—that is, the extent to which the gas must be diluted with air to become practically harmless.

3—The movements of air in ducts.

4—A synthesis of all these and related matters on a practical working scale in a vehicular tunnel constructed for this purpose in the experimental coal mine of the Bureau of Mines near Pittsburgh.

The results of these investigations will together afford the data upon which plans and designs for the ventilation of the tunnel may be intelligently based.

Problem 1 was placed in charge of Mr. A. C. Fieldner,[16,*] supervising chemist of the Bureau of Mines Experiment Station, Pittsburgh. Problem 2, of which the results are here to be summarized, was assigned to Professor Yandell Henderson of Yale University, consulting physiologist of the Bureau of Mines. The work was carried out with the collaboration of Howard W. Haggard, A. L. Prince, M. C. Teague, and R. M. Wunderlich in the Physiological Laboratory at Yale University. Problem 3 was investigated by Professor A. C. Willard of the University of Illinois. Problem 4 was supervised by Mr. A. C. Fieldner with the advice and collaboration of all concerned.

FUNDAMENTAL CONSIDERATIONS

Although carbon monoxide is the cause of more deaths than the total due to all other gases, apart from a single reaction it is a physiologically inert and nonpoisonous substance. This reaction is its combination with hemoglobin, the red coloring matter and oxygen-carrying element of the blood. To whatever extent hemoglobin is so combined, it is rendered incapable of transporting oxygen from the lungs to the tissues and organs of the body, until the carbon monoxide is again displaced. It is highly probable that all of the results of inhalation of carbon monoxide are due directly or indirectly to oxygen deficiency. Even when other toxic substances are present—as in smoke, in fumes from explosives, and in other incomplete combustions—carbon monoxide is usually the chief cause of injury or death. It acts wholly through asphyxia.

The body of an adult man of average weight contains enough hemoglobin to hold about 600 cc. of oxygen. If completely saturated, it would hold the same amount of carbon monoxide, one molecule of carbon monoxide replacing one molecule of oxygen in the blood. The absorption of 6 cc. of carbon monoxide from the lungs produces, then, 1 per cent of saturation and abolishes 1 per cent of the oxygen capacity.

The unit in which various concentrations of carbon monoxide are commonly measured and expressed for purposes of ventilation is one "part," or a certain number of "parts" of this gas mixed with 10,000 times as much air. A "part" is a hundredth of 1 per cent of an atmosphere. A man at rest breathes about 8000 cc. of air per minute, of which about 6000 cc. reach his lungs, or 60 liters in 10 minutes. Let us suppose that this air contains one part of carbon monoxide, or 6 cc. in 60 liters, and that all of this 6 cc. is absorbed. The blood would then become saturated at the rate of 1 per cent every 10 minutes per "part" of carbon monoxide in the air. Evidently the duration of exposure is a limiting factor in the amount absorbed, for one cannot absorb more than one inhales.

It appears that when a man begins breathing any low concentration of carbon monoxide mixed with air, absorption at very nearly this rate does occur, but only at first. Then the rate becomes slower. Even if the exposure is prolonged, carbon monoxide merely displaces oxygen from the blood up to a point

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[1] Received December 24, 1921.

[2] An abbreviation of a report to the Chief Engineer of the New York and New Jersey Tunnel Commissions. State of New York 1921, Legislative Document 64. Published here by permission of the Director of the U. S. Bureau of Mines and of the Chief Engineer of the Tunnel Commissions. For a more extended discussion of features of hygienic importance, see Henderson, Haggard, Teague, Prince, and Wunderlich, *J. Ind. Hgy.*, **3** (1921), 79, 137.

[*] Numbers in text refer to Bibliography.

of equilibrium depending upon the relative amounts, or mass actions, of carbon monoxide and oxygen in the air breathed and the intensity of the affinities of the two gases for hemoglobin. If thereafter the pressure of oxygen is high enough and that of carbon monoxide is low, or absent as in pure air, oxygen can likewise displace carbon monoxide and thus completely restore the oxygen-carrying power of the hemoglobin. The blood is neither directly changed nor injured by the process.

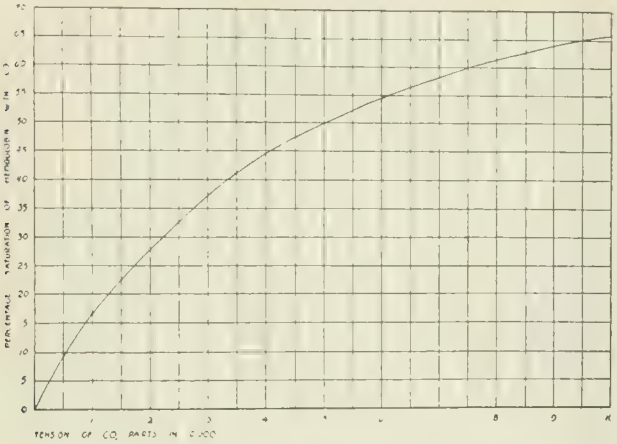

FIG. 1—FINAL OR EQUILIBRIUM DISTRIBUTION OF HEMOGLOBIN BETWEEN CARBON MONOXIDE AND OXYGEN WHEN VARIOUS LOW CONCENTRATIONS OF CARBON MONOXIDE IN AIR ARE INHALED FOR AN INDEFINITELY LONG TIME. (AFTER HALDANE)

Hemoglobin attracts carbon monoxide about 300 times as strongly as it does oxygen. Thus, if P_{O_2} and P_{CO} are the pressures of oxygen and carbon monoxide, and Hb_{O_2} and Hb_{CO} the amounts of oxyhemoglobin and carbon monoxide hemoglobin in the blood, the relations are expressed by the formula:

$$\frac{P_{O_2}}{P_{CO} \times 300} = \frac{Hb_{O_2}}{Hb_{CO}}, \quad \text{or}$$

$$\text{percentage } Hb_{CO} = \frac{P_{CO} \times 300}{P_{O_2} + (P_{CO} \times 300)};$$

or more specifically, if there are 1500 parts of oxygen and 2 of carbon monoxide, the formula works out to:

$$\frac{2 \times 300}{1500 + (2 \times 300)} = 28.5 \text{ per cent saturation with carbon}$$

monoxide.

The air in the lungs contains about 1500 parts of oxygen in 10,000. (It is actually somewhat less than 15 per cent of oxygen. The affinity of hemoglobin for carbon monoxide may also be less, or more, than 300. We are here using round numbers merely to illustrate the principle without attempting mathematical precision.) We may calculate the blood equilibrium for any concentration of carbon monoxide in the air, and from such data we may obtain the carbon monoxide dissociation curve of the blood (as shown in Fig. 1—an expression of the fundamental relations established by the investigations of J. S. Haldane).[3,4,5,6,10]

This curve indicates that, if air containing 2 parts of carbon monoxide in 10,000 is breathed for a time long enough to attain equilibrium, the blood should become about 28 per cent saturated; with 4 parts, 44 per cent; with 6 parts, 54 per cent; and so on. In the curve it is to be seen that, for instance, the equilibrium value for 10 parts of carbon monoxide in 10,000 of air is 66.6 per cent saturation, which is a sufficient degree of saturation to render a man unconscious and totally helpless. If continued, the asphyxia might lead to serious permanent injury or even death.

The question of greatest practical importance is: How long a time would be required to attain this or any other definite percentage of saturation? In other words, what is the physiological law defining the rate of absorption of carbon monoxide into the blood? From the simple calculation, given previously, regarding the oxygen capacity of the body and the volume of air drawn into the lungs, it appears that a man breathing 10 parts of carbon monoxide would inhale enough of the gas to become 66.6 per cent saturated in 66.6 minutes. But, as already indicated, the more carbon monoxide the blood contains, the greater becomes the force with which this gas tends to diffuse out again into the air. The more nearly this tendency equals and counterbalances the pressure of the gaseous carbon monoxide in the lungs, the slower the absorption of more carbon monoxide becomes. Thus to attain a condition of complete blood equilibrium many hours would be actually required; indeed, the time is indeterminate. Doubtless other factors also play a part in retarding and stopping absorption.

It appeared to us, however, that *a definite quantity for determination would be the time required for attainment of percentage saturations of one-half the equilibrium values.* Thus, in an atmosphere containing 2 parts of carbon monoxide, for which the blood equilibrium is about 28 per cent, how long a time would be required for the blood to become 14 per cent saturated? How long with 4 parts and an equilibrium value of 44, to attain 22 per cent saturation; or with 6 parts and an equilibrium of 54 to reach 27 per cent? The answer to this question is the principal practical contribution to knowledge which we have to make—namely, that *the time for attainment of half equilibrium for persons sitting at rest and breathing concentrations of carbon monoxide up to 7 parts is never considerably less than one hour.* This fact is, we believe, of fundamental importance for ventilation engineering. We have established it purely experimentally. It might easily be correlated with the oxygen consumption and the carbon dioxide elimination, but we have not thought this to be of practical importance to the immediate object of this report. It does not, nor does it aim to, express what the average person does under the conditions, for many of our subjects fell much below this rate of absorption. None exceeded it. The value of the rule is that it expresses the worst attainable, or, so to speak, the "maximum load."

We may here conveniently consider the question, often raised, of possible extreme individual susceptibility. Such susceptibility might conceivably arise: (1) from anemia, that is, a subnormal amount of hemoglobin; (2) from an unusual avidity of the individual's hemoglobin for carbon monoxide; (3) from unusual susceptibility to the ill effects of oxygen deficiency; or (4) from a volume of breathing much above the ordinary. The first is unimportant practically, inasmuch as anemics need not spend long periods in ill-ventilated garages, nor ride through tunnels on slow moving trucks. If, however, they are transported at the speed of a passenger car or an ambulance through a two-mile tunnel containing the average concentration of carbon monoxide here to be proposed, the time of exposure will be too brief to allow an absorption sufficient for any considerable ill effects. The second possibility has been investigated by us, but has not been found to occur. (Owing to their highly technical and space-consuming character, these studies are omitted here, but appear in the full report.)

There is reason to believe that there are individual differences in the degree of the ill effects induced by considerable oxygen deficiency. Aviators and mountain climbers exhibit such differences, and in our more extreme tests headache has occurred in some persons at a somewhat lower percentage saturation of the blood than in others. We have, however, found no one who experienced this effect—the first sign of oxygen deficiency—under the conditions of the standards we shall propose.

The volume of breathing is by far the most important element in the rate of absorption of carbon monoxide and thus in the individual variations in the ill effects of inhalation of this gas. In general, the expired air of a healthy man contains 4 or 5 per cent of an atmosphere less oxygen than the inspired air, and this percentage deficit is nearly the same during rest with a breathing of 8 liters and under physical exertion with a respiration several times as large. In other words, the volume of breathing is roughly proportional to the amount of the oxidation and energy liberation occurring in the body. In our observations, persons of vigorous physique and large breathing rates have absorbed carbon monoxide much more rapidly, as measured in percentage blood saturation, than those of more sedentary habit and delicate physique. As the standard which we shall propose is one adjusted to protect even the strong, it will therefore afford an extra safeguard to the weak and sick, who breathe little (except in febrile cases) and who would, accordingly, absorb carbon monoxide comparatively slowly. Only in the case of children, whose active vitality involves a relatively large food and oxygen consumption and a corresponding volume of breathing, will this rule probably not hold. But even for the most active child, a period of exposure of only 10 or 15 minutes to the concentration of carbon monoxide here approved will not be long enough for any considerable absorption of the gas.

The particular problem before us—that of a standard for the ventilation of the proposed vehicular tunnels under the Hudson River—may, therefore, be thus simply expressed: What percentage saturations of the blood with carbon monoxide cause appreciable discomfort in healthy men sitting at rest, and what percentage saturations do not? The answer to this question, the probable duration of exposure of passengers through the tunnel, and the law of carbon monoxide absorption as above stated, are the three considerations on which any sound standard must be based.

In view of the foregoing discussion it is, we trust, clear that standards of concentrations, which will adequately protect men exposed for the greater part of an hour, will afford an enormous factor of safety for persons inhaling the vitiated air for only 10 or 15 minutes. We are informed by the engineers that all traffic through the tunnels will be in two distinct classes—namely, passenger cars, which will make the trip in 10 or 12 minutes, and trucks which may take as long as 35 or 40 minutes. The standards which we set ourselves to work out are such as will afford not only absolute safety but also complete freedom from any trace of discomfort for healthy and vigorous adults exposed for periods of 45 to 60 minutes.

EXPERIMENTS ON MEN IN SIX CUBIC METER CHAMBER

The method of studying the effects of various concentrations of carbon monoxide upon which we have chiefly relied for establishing our standard is illustrated in Fig. 2. It involves a chamber of 6.4 cubic meters (226 cubic feet) capacity, the walls and door of which are covered with galvanized sheet iron with soldered joints. The door is easily made gastight by placing long strips of broad (2-inch) adhesive plaster over the cracks along lintel, jambs, and sill. The chamber holds any concentration of gas for a day without appreciable loss from diffusion through undiscovered leaks. A small hole in the door, covered by a piece of adhesive plaster, allows the hand of the subject to be thrust outside for the withdrawal of blood.

Into this chamber are introduced measured amounts of pure carbon monoxide, made by dripping formic acid into strong sulfuric acid and distilling it by gentle heat into a large bottle filled with water, which the gas displaces. The concentration of gas desired in the chamber is obtained by running into the bottle 640 cc. of water per part of carbon monoxide desired, and thus displacing this volume of gas from the bottle into the chamber. An electric fan in the chamber insures immediate and complete mixing. In our experiments, two checks on the concentration of gas in the chamber were obtained: (1) By analysis of the carbon monoxide, before it was introduced, by means of a modified Orsat apparatus, and ignition with an electrically heated platinum spiral; and (2) by analysis of a mixed sample of the air from the chamber by the iodine pentoxide method, or by means of diluted blood. (For a description of these analytical methods, see bibliographical references 1, 2, 3.)

In this chamber, in turn, the members of the staff of this investigation and a few other persons spent periods of one hour after amounts of carbon monoxide from 2 to 8 parts, and in one case, 10 parts, had been introduced. While the subjects sat and read most of the time, there were a sufficient number of acts—such as turning on the electric fan, standing up to look out of the window for a moment, opening and closing flasks to take air samples for later analysis, etc.—to correspond fairly well with the activity of the driver of a car. When we speak of the absorption of carbon monoxide by a person "sitting at rest," the condition must, therefore, be understood as only such moderate rest as this.

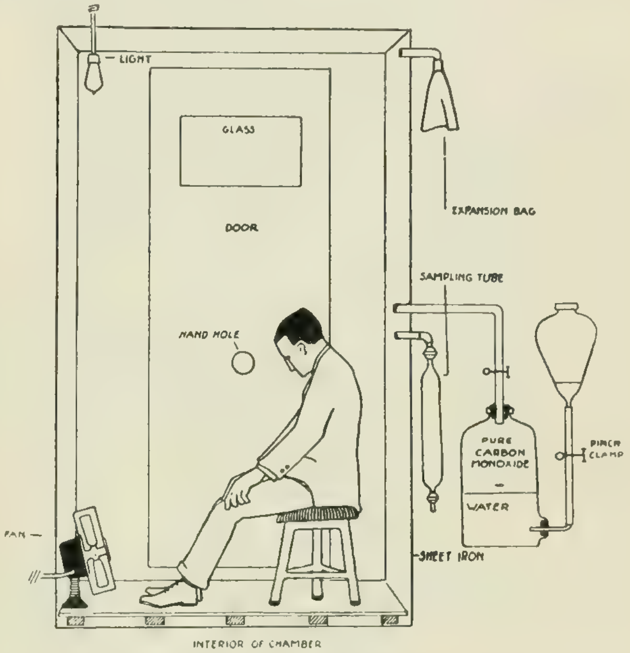

FIG. 2—SIX CUBIC METER CHAMBER AND APPARATUS FOR INTRODUCING MEASURED AMOUNTS OF CARBON MONOXIDE

Blood, to the amount of twenty or thirty drops, was drawn from a finger before the subject entered the chamber; and 0.02 cc. was drawn at the middle of the period and at the end, and usually once or twice during the next 3 hours. These blood samples were analyzed for carbon monoxide by the carmine titration method.[3]

After the subject had been out of the chamber for a few minutes, the tension of carbon monoxide in his lungs, supposedly in equilibrium with the blood, was determined by breathing back and forth several times, during 20 to 30 seconds into a rubber bag. Football, or basket ball, "bladders" were used for this purpose. (A series of check determinations on four subjects showed that the maximum concentration of carbon monoxide from these bags was reached in five rebreathings during 30 seconds.) This air was then analyzed for carbon monoxide by the iodine pentoxide method, or the blood carmine method. The subject's volume of resting breathing was determined either in or outside of the chamber by means of a mouth-piece, nose clip, double valves, Douglas bag, or gas meter; and the volume per minute was calculated.

In some experiments the respiration was increased by exercise, and the increase was measured and correlated with the correspondingly greater absorption of carbon monoxide. In these experiments the subjects did "stationary" walking or running in the chamber by lifting the feet and stamping. The exertion involved is considerable, but with care it can be kept quite uniform for half an hour at a time. The pulse was counted in the chamber, and before and after the test. The effects on the pulse and respiration of running up and down four flights of stairs, each 12 feet vertically, were also determined before and after the period in the chamber.

In a few cases the retinal fields were determined and plotted. With the degrees of anoxemia occurring in these experiments, however, the effects on vision in this respect were unimportant. The Romberg test, the ability to stand erect with eyes closed without wavering, was also used. In some cases after an hour in eight parts of carbon monoxide, it showed marked loss of equilibrium.

But of all signs and tests, both in the experiments in the small chamber here under discussion and in those that are to be described in the next section, the typical carbon monoxide, or oxygen deficiency, headache proved most definite and reliable. It is a distinctly localized pain, usually frontal, throbbing, intensified by lying down or by exertion. It is sometimes accompanied by more or less nausea, readily increasing to vomiting. The mind is not clear, except with an effort, and one's surroundings seem a little strange. The temper is easily upset, very much as in alcoholic intoxication, and the judgment is likely to be bad. There are wide variations in the degree of this headache, but in the experiments discussed in this section it was never extreme. On the border line it verged merely into slight lassitude. As a criterion of the effect of carbon monoxide, however, it is more distinct than any artificial test. Concentrations of gas too weak and periods of exposure too short to induce this sign in anyone may be considered entirely harmless.

From Table I, in which the data of thirty-two experiments performed in this way on nine men and one woman are summarized, it appears that *no one had an appreciable degree of headache after a period of 1 hour in the chamber with 4 parts of carbon monoxide* or less, and that with 6 parts the effect, if any, was usually very slight. With 8 parts there was decided discomfort for some hours, although not enough to interfere with efficient work in the laboratory or at the desk. After an hour in 10 parts even an unusually resistant subject (Y. H.) was decidedly miserable and averse to work for 5 or 6 hours, and could still recognize the effects after 12 hours. Examination of these data enables us to reach a working rule regarding the rate of absorption of carbon monoxide, for we find that up to and including concentrations of 6 parts of carbon monoxide in 10,000 of air the figures in Column 5 of Table I do not exceed values of about one-half those for complete equilibrium given in Column 3 and drawn from Fig. 1.

TABLE I—SUMMARIZING EXPERIMENTS ON MEN IN SIX CUBIC METER CHAMBER

Number of Experiments	Parts CO in 10,000 of Air Breathed	Corresponding Equilibrium Value of the Blood in Percentage Saturation	Observed Saturation in the Blood after 1 Hr. Minimum	Observed Saturation in the Blood after 1 Hr. Maximum	Headache and Other Symptoms
2	2	28	11	12	None
3	3	37	10	14	None
11	4	44	14	22	None
9	6	55	18	26	None in 7 Slight in 2
4	8	62	26	32	Marked in all 4
1	10	67	38	..	Severe

In other words, during one hour sitting at rest in such atmospheres, a man's blood never absorbs appreciably more than half the amount of carbon monoxide which it would take up if he stayed in the atmosphere indefinitely. Inactive and small breathing persons absorb less. At concentrations of 8 and 10 parts of carbon monoxide the figures deviate slightly from this rule, but the rule of half saturation appears to be safe and convenient up to 7 parts. From the experiments in which work (stationary walking) was performed in the chamber it appears that a man who exercises sufficiently to double the volume of breathing absorbs as much carbon monoxide in half an hour as he does at rest in one hour. We have found in other experiments, that when walking fast a man breathes about twice as much air (with a corresponding energy expenditure and oxygen consumption) as when sitting still, and that when hurrying or doing rather heavy manual labor he breathes about three times as much, and under exertion even more. These figures may be directly applied to conditions as they occur in regard to absorption of carbon monoxide. The estimation of the time required for half equilibrium must be shortened accordingly.

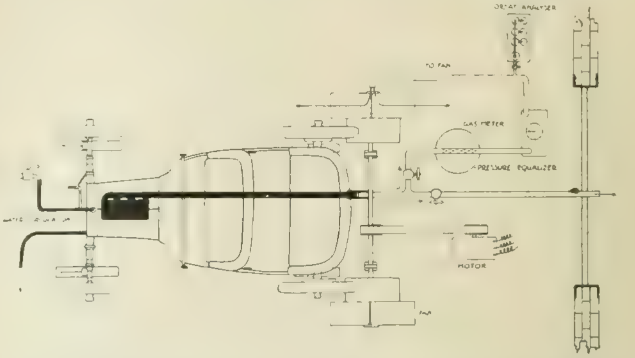

FIG. 3—APPARATUS IN LARGE GASSING CHAMBER FOR PRODUCING EXHAUST GAS UNDER CONDITIONS SIMULATING THOSE IN A VEHICULAR TUNNEL

ELIMINATION OF CARBON MONOXIDE—As regards the elimination of carbon monoxide after gassing, our data show that the process is not complete until one or two hours, or even longer, after return to fresh air. Roughly, the rate of elimination is 30 to 50 per cent per hour, depending doubtless on bodily activity and the volume of fresh air breathed.

OBSERVATIONS IN LARGE GASSING CHAMBER

The experiments above described involve exact, but rather artificial conditions. Exhaust gas is not pure carbon monoxide and the number of persons who could be tested in the 6 cubic meter chamber was quite limited. It appeared essential, therefore, to obtain confirmatory observations under as nearly real conditions and on as many persons as possible. For this purpose a brick building, 30 feet square, with walls 12 feet high at the side, and a hip roof, was erected. Its cubic capacity was approximately 12,000 cubic feet of air, which is about the volume of a section of the vehicular tunnel which will contain one car when the traffic is active.

A Ford car was installed (as shown in Fig. 3) near the middle of this chamber, with a continuous stream of water running into and out of its radiator to prevent overheating. The axles were supported on a wooden framework so that the rear wheels turned clear of the ground. Against them were pressed two large wooden pulley wheels on a piece of heavy shafting, at the ends of which were wooden paddle wheels. The engine of the car, therefore, ran with a fair load, and the power was expended in mixing the air in the chamber. The paddle wheels did this so effectively that in a number of tests practically uniform concentrations of exhaust gas were found simultaneously in all parts of the chamber.

The exhaust of the car was connected to a 2-inch iron pipe with a T and two valves. From one valve a pipe led to a gas meter, and discharged close to one of the paddle wheels, which drew in and distributed the gas. The pipe from the other valve led outside of the building. Thus, by adjusting the valves, all or any part of the exhaust gas could be discharged into the chamber, and this volume read on the meter. Samples of the exhaust gas unmixed with air were analyzed for carbon monoxide in an Orsat apparatus, with ammoniacal cuprous chloride as the absorbent. The percentage ranged between 5.5 and 6.8 per cent with an average of about 6 per cent. The engine discharged a total of about 25 cubic feet of exhaust gas per minute, from which we calculated that approximately 1.5 cubic feet of carbon monoxide were produced by the car per minute.

Diffusion from the chamber through the walls and roof, and through cracks around the doors and windows, was considerable. Whenever the engine was stopped, there was thus a drop of about one-third of the concentration of carbon monoxide in 15 minutes. Usually the entire exhaust of the engine was discharged through the meter into the chamber until the desired concentration of carbon monoxide was approximately reached. Thereafter, a part of the gas was discharged out of doors, and only enough was passed into the chamber through the meter to compensate for loss by diffusion. Samples of the air in the chamber were taken at intervals during the period of exposure, and the amount of carbon monoxide determined either by means of iodine pentoxide (with a correction for vaporized gasoline) or by the blood carmine method, or in both ways. Some discrepancies occurred in the analytical data, but it must be kept in mind that the methods were difficult and the amounts of the substance were minute far beyond the range of ordinary gas analysis.

With practice, considerable facility in controlling the concentration of carbon monoxide in the chamber was attained. The experimental conditions were quite realistic. The car was old and had had rough treatment, and the engine was somewhat irregular in action. The exhaust gas was, therefore, contaminated with at least as much gasoline, oil and soot, and other substances, in addition to water vapor, carbon monoxide, and carbon dioxide, as may be met with in any well-regulated vehicular tunnel. Owing to the fact that vaporized gasoline and other constituents of exhaust gas beside carbon monoxide act upon iodine pentoxide (the condensation of these vapors by means of liquid air had not then been worked out), the figure 0.6 was determined as the factor by which it was necessary to multiply the iodine liberated in analysis of chamber air for the estimation of the carbon monoxide.

Two Typical Experiments in Large Gassing Chamber

Protocol 1

The atmosphere in the chamber gave on analysis 4 parts of CO in 10,000 of air over the entire period of 1 hour. Eight subjects were exposed to this for the full hour. For the most part they were seated. The approximate percentage saturation of the blood with carbon monoxide (per cent HbCO) was determined indirectly from analysis of the alveolar air from the lungs, obtained by breathing back and forth several times from and into a small rubber bag.

Subjects	Sex	Per cent HbCO	Headache and Other Symptoms
C. P.	Male	18	None
E. S.	Male	17	None
E. W.	Male	21	None
M. H.	Female	20	None
M. B.	Female	20	None
E. H.	Male	18	None
E. L.	Male	17	None
M. S.	Male	20	None

Protocol 2

The atmosphere in the chamber gave on analysis an average of 9 parts of CO in 10,000 of air. Seventeen subjects were exposed to this for the full hour. For the most part they were actively walking about. The percentage saturation of the blood with CO was estimated as in the previous protocol.

Subject	Sex	Per cent HbCO	Headache and Other Symptoms (as Reported by Subjects)
E. G.	Male	35	Dizziness, headache, and some nausea
A. V.	Male	37	Throbbing headache, general lethargy for 24 hrs.
A. D.	Male	30	Headache, nausea, and chills
J. O.	Male	29	Short period of dizziness, severe headache for 9 hrs
L. P.	Male	27	Throbbing headache for 9 hrs.
M. O'C.	Male	37	Severe headache for 6 hrs.
J. F.	Male	35	Severe headache, vomited, in bed 5 hrs.
E. W.	Male	35	Severe headache for 20 hrs.
M. G.	Male	35	Severe headache for 5 hrs.
H. F.	Male	29	Severe headache for 8 hrs.
E. T.	Male	33	Nausea and severe headache for 7 hrs.
E. S.	Male	28	Headache for 8 hrs.
H. B.	Male	30	Severe headache and some nausea for 6 hrs.
H. L.	Female	30	Nausea and violent headache for 48 hrs.
E. W.	Male	27	Headache for several hours
A. W.	Male	28	Headache and some nausea
P. S.	Male	30	Severe headache and vomiting
J. S.	Male	28	Severe headache for 72 hrs.

In this chamber groups of a dozen or more persons at a time sat or moved about for periods of one hour. In addition to the staff of this investigation a number of students of the Yale Medical School served as subjects. We take this opportunity to recognize the intelligent and valuable service rendered by these young men and women.

After the tests the general condition and feelings of the subjects, particularly the occurrence or absence of headache, were noted. When the subjects had breathed fresh air for 5 minutes after leaving the chamber, samples of lung air, obtained by having them rebreathe repeatedly into a small rubber bag, were analyzed for carbon monoxide. In such analyses the gas found is that which has diffused out of the blood into the lung air, and the analytical data indicate, therefore, the tension (partial pressure) of the carbon monoxide in the blood. The effect of running up and down four flights of stairs was also noted, as exercise markedly intensifies asphyxial symptoms. We have repeatedly seen fainting induced by a less exertion after one hour of moderate activity in 10 parts of carbon monoxide.

Only two typical protocols of these tests can be given in this abbreviation of our report, but the whole of the data may be summarized by the statement that, so long as the standard worked out in the previous section was not exceeded, no appreciable ill effects were induced in any of the numerous subjects. Above this standard, however, headache resulted in nearly all cases, and in some persons nausea and vomiting also occurred.

Confirmatory Experiments

Some confirmatory observations were also made in public garages, and in the taxicab stand under the Grand Central Railroad Station, New York City.

EXPOSURE OF HORSES TO EXHAUST GAS—A few observations were made on two U. S. Army artillery horses. They were of the Percheron breed and weighed between 1400 and 1800 pounds, one bay and the other white. We are greatly indebted to Colonel R. E. D. Hoyle, Commanding Officer, Field Artillery Unit, R. O. T. C., stationed at Yale University, for the loan of the animals.

The car was taken outside of the tunnel gassing chamber and the exhaust gas piped to the inside. The horses were not hitched, but were allowed to move about freely inside the chamber. In each experiment a blood sample was drawn from the ear before and after gassing. The results obtained corresponded fairly closely with those on man.

The Rule of Half Equilibrium Value in One Hour

From well-established theory, as discussed above, and from the foregoing experiments, we have these data:

1—A curve (Fig. 1), which expresses the equilibrium relations between the partial pressure of CO in air and the percentage saturation of the hemoglobin of blood freely exposed to such air.

2—The rule that one hour may be used as the (minimum) period for attainment of one-half the equilibrium degree of blood saturation for a person at rest.

3—The fact that this period varies inversely as the energy expenditure and corresponding volume of air breathed.

4—The fact that for an exposure of one hour, 18 per cent saturation of the blood does not produce even a slight headache. For exposures of several hours, we have adopted for various reasons 12 per cent saturation (full equilibrium to 0.6 part per 10,000 of air) as the figure which would produce no appreciable decrease of comfort or efficiency.

These data are combined in Fig. 4. The two scales at the left show the corresponding values for CO in blood and CO in air, the ordinates and abscissae, respectively, of Fig. 1. The curves show the rate at which, as calculated from the half saturation rule, the blood would absorb CO when a man at rest breathes atmospheres of this gas of 1 to 7 parts in 10,000 of air. The time element is indicated below the abscissa in three scales according as the subject is sitting, walking, or working moderately. Horizontal dotted lines have been drawn at the levels of freedom from discomfort for exposures of one hour, and for exposures of several hours.

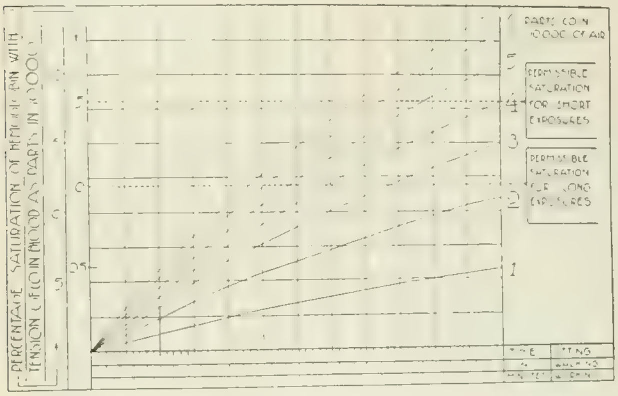

Fig 4—Curves Showing Maximum Rate of Absorption of Carbon Monoxide by the Blood in Persons Exposed to Concentrations up to Seven Parts of Carbon Monoxide in 10,000 of Air, for Periods up to 1 Hour, during Rest (Sitting), and for Shorter Periods of Walking and Working. For Discussion See Text

The way in which this diagram may be used is illustrated in Fig. 5. It is here supposed that the subject walks with the air current for 35 minutes while the CO increases gradually up to 7 parts per 10,000 of air. The small triangles show the increments of CO absorbed by the blood each in 5-minute intervals, and the total which might be reached. If the subject were sitting at rest in a car the triangles would be correspondingly smaller. If he were working hard they would be larger. If he were traveling against the air current the absorption and triangles would be largest at first and then progressively smaller. It is to be noted that the time element is the sum of all the bases of all the triangles, and not merely the abscissa of the highest concentration reached.

It is evident from this diagram that if at any point the concentration exceeds 6 parts of monoxide in 10,000 of air, men doing hard work for even a short time will be unfavorably affected. On the other hand, the curves show that passengers in cars going through the tunnel in 10 or 15 minutes will absorb very little carbon monoxide—a factor of safety which is, we believe, sufficient to afford ample protection for children and invalids. *The standard which we propose for exposures of 45 minutes—4 parts in 10,000 or its equivalent in an average of concentrations from 0 up to 6 in 10,000—affords, in the light of our experiments, not only complete safety but also an assurance of freedom from disagreeable effects.* Risk of considerable discomfort would begin at 8 to 10 parts of carbon monoxide in 10,000 of air in periods of one hour during rest and for shorter periods during exertion. Actual danger would begin with concentrations not very much higher and periods not very much longer. The point should be emphasized, however, that we are dealing only with a standard of chemical purity of the air. Other features of tunnel ventilation as, for example, wind velocity, moisture, temperature, etc., are not included in the standard here defined, nor is comfort in these respects assured by it.

The whole matter may be even more simply summed up in an expression involving the time measured in hours, the concentration of carbon monoxide in the air in parts in 10,000, and a constant for each degree of physiological effect. The physiological effects of all concentrations and times (within reasonable limits, that is, a few hours) may be then defined as follows:

1—Time × concentration = 3, no perceptible effect.
2—Time × concentration = 6, a just perceptible effect.
3—Time × concentration = 9, headache and nausea.
4—Time × concentration = 15, dangerous.

Physical exertion and increased breathing would reduce the constant in the first equation from 3 to 2, or 1, or even less, and would affect the other equations correspondingly.

Concordance of the Standard Here Proposed with the Observations of Other Investigators

The standard defined in Fig. 4 may seem, from the work of others, especially that of Haldane, unduly high, if one fixes attention upon the concentration of carbon monoxide in the air breathed; or it may appear unnecessarily low, if stated in terms of the maximum percentage saturation, *i. e.*, complete equilibrium of the blood and the corresponding tension. The work of Haldane is so preëminent in this field, alike in amount, thoroughness, and practicality, that discordance between the conclusions drawn from his investigations and the standard here proposed would require elaborate explanation and defense. In fact, however, we believe that when all aspects of the question are taken into consideration, our observations, and conclusions, although differing in detail, are essentially concordant with those of Haldane.[4,5] Briefly stated, his principal conclusions were as follows:

> The symptoms caused by carbon monoxide depend upon the extent to which the hemoglobin has been saturated. The symptoms are due solely to the deficiency of the oxygen percentage in the blood.
>
> When air containing carbon monoxide is breathed, about half of the carbon monoxide actually inhaled is absorbed, except toward the end of the process when absorption is coming to a standstill.
>
> The rate of absorption and time required for symptoms to appear is proportional to the respiratory exchange and may be very much shortened by the increased breathing of exercise.
>
> The symptoms do not become appreciable during rest until the blood is about a third saturated. An individual in this condition suffers from palpitation and throbbing in the head and is liable to become faint or dizzy on any exertion, such as that of ascending stairs, or on sudden exposure to cold air.

In experiments on himself Haldane[6] found that, when 50 per cent saturated, he could scarcely stand and could not walk alone without falling down. There was giddiness, dullness of the senses, distinct shortness of breath, and labored breathing. In the course of 2 or 3 hours after leaving the contaminated air he found that nearly all of the carbon monoxide disappeared from the blood, which had then returned to its normal condition. Headache lasting for some hours was likely to ensue from the exposure if the latter were sufficiently long.

In reporting on the conditions which should be maintained in the Underground Metropolitan Railways of London,[7] he said:

> Roughly speaking, the probable action on a healthy person of varying percentages of carbon monoxide in the air may be stated as follows: 2.5 volumes per 10,000 would suffice after a sufficient time (after an hour and a half during rest, but very much less during even slight exertion) to cause symptoms just distinctly appreciable on exertion. Five volumes per 10,000 would cause marked dizziness or fainting on exertion, 9 volumes would cause inability to walk, and about 15 volumes might produce death. * * * * Considering the enormous number of people in various states of health who use the railway, * * * * it seems desirable that not more than one volume per 10,000 of this gas should be present in the air.

To these statements may be added the fact that Burrell[8] found that after breathing air containing 25 parts of carbon monoxide per 10,000 of air for 20 minutes he had at first only a slight headache, but later became ill. The illness lasted for several hours and was accompanied by nausea and headache.

Obviously when Haldane recommended a standard of 1 : 10,000 he had in mind prolonged exposure. If, however, we turn to the more fundamental physiological conditions—namely, that of the percentage saturation of the blood—the apparent discrepancy between his recommendation (1 : 10,000) and ours (4 : 10,000) disappears. Thus, a glance at Fig. 4 shows that 50 minutes, a much longer time than any one will be exposed in passing through the Hudson River Tunnel, in an atmosphere containing 4 parts of carbon monoxide in 10,000 could induce only 16 per cent blood saturation. Now, from Fig. 1, blood which is 16 per cent saturated would be in full equilibrium with about 1 part of carbon monoxide in 10,000 of air. In other words, a stay of many hours in an atmosphere of 1 part of carbon monoxide in 10,000 of air would involve the same percentage saturation as a stay of 50 minutes in 4 parts per 10,000. Indeed, as the development of symptoms from carbon monoxide is wholly a question of oxygen deprivation, it is safe to assert that even a somewhat greater saturation of the blood lasting for only a short period would involve less physiological ill effect than a prolonged period, involving nearly full equilibrium, in 1 part per 10,000 of air.

Finally, we may here quote from a letter received from Dr. Haldane, which was in answer to a letter from us stating the general trend of our observations and findings, and in which Dr. Haldane says:

> In the report on the Underground Railway the chemical standard which I recommended if steam traction was continued was 0.15 per cent of carbon dioxide, and I pointed out that this would contain about 0.01 per cent carbon monoxide. But the standard was not based primarily on the carbon monoxide, but on the general unpleasantness of the air. There was no definite evidence of people being upset by the carbon monoxide, though there was often 0.03 to 0.05 per cent at certain parts of the tunnel and stations; and I even found 0.066 per cent of carbon monoxide (with 0.89 per cent of carbon dioxide) on the platform of Gower Street Station (near University College). Passengers were never exposed long enough for ill effect and the men at the stations were probably more or less acclimatized.* * * *
>
> What I should now say is that with long exposures of several hours anything more than 0.02 per cent should be avoided. For exposures of less than an hour 0.05 per cent would not be really objectionable. As regards gases from motors, however, the smoke and smell might possibly be worse than the carbon monoxide. On this point I have no experience, though I have run across cases of poisoning where there does not seem to have been much smoke or smell.
>
> You will probably see from the above that my ideas about carbon monoxide coincide very closely with what your experiments point to.* * *

Comparative Toxicity of Pure Carbon Monoxide, Illuminating Gas, Exhaust Gas from Gasoline, Exhaust Gas from Coal Distillate, and Gasoline Vapor

The general agreement between the experiments with pure carbon monoxide mixed with air in the small chamber and the results with exhaust gas in the large chamber indicates strongly that in the concentrations occurring in the latter (and thus in any garage or tunnel) carbon monoxide may be taken as the only substance of sufficient toxicity, and present in sufficient amount, to have any considerable physiological effect. All of the data in both of these series of experiments were, however, based upon low concentrations of the gas and the deductions from them might not apply equally to high and lethal concentrations.

We have, therefore, thought it well to check these results by means of observations on animals in high concentrations of gas. For this purpose dogs were used. The animal in each case was placed in a cube-shaped plate glass chamber measuring about 3 feet on a side. The gas to be tested was mixed with air in a gasometer of several hundred liters capacity, so that the carbon monoxide concentration was about 0.3 to 0.4 per cent, or 30 to 40 parts in 10,000. From the gasometer the gas mixture was passed into the chamber through a tube by a small electrically driven air blower. Another tube from the chamber led outdoors. Usually the gas was run in at such a rate that the animal was at the point of death in 30 to 35 minutes. The animal was then removed from the chamber and a sample of blood was drawn, and analyzed by the carmine titration method.

EXPERIMENTS WITH PURE CARBON MONOXIDE MIXED WITH AIR—In this atmosphere the animals became unconscious with no more apparent discomfort than if anesthetized with ether. The blood of five dogs at the point of death contained the following percentages of carbon monoxide: 87, 82, 84, 79, 88; average, 84.

EXPERIMENTS WITH ILLUMINATING GAS, FATTENED WATER GAS, MIXED WITH AIR—In such an atmosphere the symptoms during intoxication differed in some respects from the preceding group. There occurred in all cases more rapid collapse and distinctly greater respiratory excitement. Nausea and vomiting, which were lacking in the experiments with pure carbon monoxide, occurred in all the animals of this second group. These observations and the fact that death ensued with a lower percentage of carbon monoxide in the blood indicate that illuminating gas contains some substance or substances which render it distinctly more toxic than an equal amount of pure carbon monoxide. The blood of the five dogs used in these experiments contained at the point of death the following percentages of carbon monoxide: 74, 67, 76, 71; average, 72.

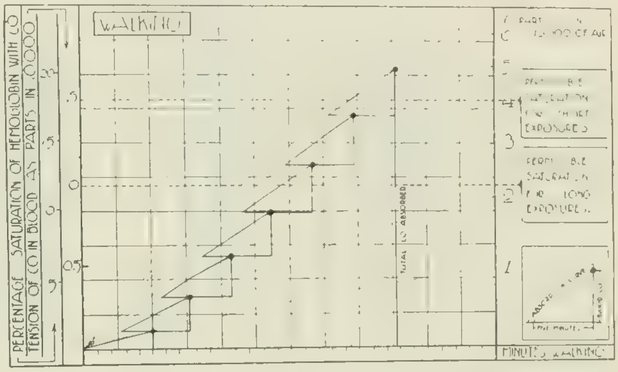

Fig 5—Illustration of Method for Applying Absorption Curves to Specific Conditions Arising in a Vehicular Tunnel. Longitudinal Ventilation. Subject Walking in Direction of Air Current

EXPERIMENTS WITH EXHAUST GAS FROM A CAR USING GASOLINE—For these tests the three commonest varieties of gasoline sold locally were used successively. A large rubber bag was attached to the exhaust of a car (one in good condition, with an efficient and smooth running engine), while it was standing with the engine running "idle." This gas was analyzed for carbon monoxide by means of an Orsat apparatus in the usual way. The gas was then mixed with air in the large gasometer to approximately the same concentration of carbon monoxide as in the previous experiments and was then administered to animals in the glass chamber. In these experiments the animals were at the point of death in approximately the same time as in the first series of experiments. The symptoms were similar to those from pure carbon monoxide and unlike those from illuminating gas. The percentages of carbon monoxide in the blood were also similar to the first series, but higher than the second. Evidently carbon monoxide was here practically the only toxic substance. The blood of the five dogs in this group of experiments contained at the point of death the following percentages of carbon monoxide: 84, 86, 83, 81, 81; average, 83.

EXPERIMENTS WITH EXHAUST GAS FROM A CAR USING COAL DISTILLATE—Two dogs were exposed to this gas, exactly as the animals had been exposed in the previous experiments to exhaust gas from gasoline, and died with symptoms like, but more marked than, those of the dogs poisoned with illuminating gas. The blood of these two animals had a decided brownish tinge indicating a marked destructive influence upon the hemoglobin of the blood. It is known that benzene has such an effect.

The composition of the coal distillate, according to figures kindly furnished by the chemist of the Gas Company, was:

	Per cent
Benzene	69.0
Toluene	15.5
Solvent naphtha	13.5
Heavy naphtha	2.0
TOTAL	100.0

The blood of the two dogs used in these experiments contained at the point of death the following percentages of carbon monoxide: 60, 64; average, 62.

EXPERIMENTS WITH GASOLINE VAPOR[9]—In order to determine the possible part which unburned gasoline vapor might play as a toxic constituent of exhaust gas, dogs were exposed to the vapor of carefully controlled concentrations. It was found that 100 parts of gasoline vapor in 10,000 of air caused convulsions and 250 parts resulted in death. Obviously unburned gasoline is not an appreciable factor in the effects of exhaust gas, but the vapor contained in a tank from which gasoline has been drawn, and even after considerable ventilation, would be highly toxic—as the practical experience of the industry fully confirms.

PRINCIPAL CONCLUSIONS

The general standards at which we arrive for periods of a few hours are: When the time in hours multiplied by the concentration of carbon monoxide in parts per 10,000 of air equals 3, there is no perceptible physiological effect. When it equals 6, there is a just perceptible effect. When it equals 9, headache and nausea are induced. When it equals 15 or more, the conditions are dangerous to life.

If the volume of breathing is increased by exercise (even by slow walking, and correspondingly more by physical work) the rate of absorption of carbon monoxide is increased proportionally.

After return to fresh air, the elimination of carbon monoxide through the lungs proceeds at a rate of 30 to 60 per cent reduction of the blood saturation per hour.

In the exhaust gas from gasoline, carbon monoxide is the only considerable toxic constituent. In the exhaust gas from coal distillate (benzene, etc.), and in illuminating gas, there are present accessory toxic substances.

BIBLIOGRAPHY

1—M. C. Teague, "Determination of Carbon Monoxide in Air Contaminated with Motor Exhaust Gas," *J. Ind. Eng. Chem.*, **12** (1920), 964.

2—H. Kreisinger and F. K. Ovitz, "Sampling and Analysis of Flue Gases," Bur. Mines, *Bull.* **97** (1915), 21, 32.

3—J. S. Haldane, "Methods of Air Analysis," London, Charles Griffin and Co., **1912**, 107.

4—C. G. Douglas, J. S. Haldane, and J. B. S. Haldane, "The Laws of Combination of Haemoglobin with Carbon Monoxide and Oxygen," *J. Physiol.*, **44** (1912–1913), 275.

5—J. S. Haldane and J. Lorrain Smith, "The Mass and Oxygen Capacity of the Blood in Man," *J. Physiol.*, **25** (1899–1900), 331.

6—J. S. Haldane, "The Action of Carbonic Oxide on Man," *J. Physiol.*, **18** (1895), 430.

7—Report of the Board of Trade on the Ventilation of the Metropolitan Railway Tunnels. *Parliamentary Paper* **C8684** (1897).

8—G. A. Burrell, "The Use of Mice and Birds for Detecting Carbon Monoxide after Mine Fires and Explosions," Bur. Mines, *Tech. Paper* **11** (1912).

9—H. W. Haggard, "The Anesthetic and Convulsant Effects of Gasoline Vapor," *J. Pharmacol.*, **16** (1920), 401.

10—Y. Henderson, "Carbon Monoxide Poisoning," *J. Am. Med. Assoc.*, **67** (1916), 580.

11—Y. Henderson and H. W. Haggard, "The Elimination of Carbon Monoxide from the Blood after a Dangerous Degree of Asphyxiation and a Therapy for Accelerating the Elimination," *J. Pharmacol.*, **16** (1920), 11.

12—H. W. Haggard, "Studies in Carbon Monoxide Asphyxia. 1—The Behavior of the Heart," *Am. J. Physiol.*, **56** (1921), 390.

13—H. W. Haggard and Y. Henderson, "The Treatment of Carbon Monoxide Poisoning," *J. Am. Med. Assoc.*, **77** (1921), 1065.

14—H. W. Haggard, "Studies in Carbon Monoxide Asphyxia. 2—The Growth of Neuroblasts in the Presence of Carbon Monoxide; a Demonstration of the Non-toxic Action of This Gas on Nervous Tissue," *Am. J. Physiol.*, **1921** (in press).

15—J. S. Haldane, "Respiration," Yale University Press, **1922**.

16—A. C. Fieldner, A. A. Straub and G. W. Jones, *J. Ind. Eng. Chem.*, **13** (1921), 51.

A. C. S. Lecturers at West Point and Annapolis

From the data submitted to the authorities, the following speakers have been selected to address the United States Military Academy and the United States Naval Academy on the dates mentioned:

U. S. MILITARY ACADEMY

April 5—"Chemical Agents in Battle," MAJOR E. J. ATKISSON, Chemical Warfare Service, Edgewood Arsenal, Md.

April 12—"The Manufacture, Chemistry, and Uses of Rubber Goods," MR. W. C. GEER, Vice President, B. F. Goodrich Co., Akron, Ohio.

April 19—"Motor Fuels Ten Years Hence," PROF. RALPH H. MCKEE, Columbia University, New York, N. Y.

April 26—"Helium, Its History, Properties, and Use in Aeronautics," DR. R. B. MOORE, Chief Chemist, Bureau of Mines, Washington, D. C.

May 3—"The Role Played by Cellulose in the Late War,' PROF. HAROLD HIBBERT, Yale University, New Haven, Conn.

U. S. NAVAL ACADEMY

February 25—"Nitrogen Fixation and Its Relation to the Production of Food and Explosives," DR. ALFRED H. WHITE, Professor of Chemical Engineering, University of Michigan, Ann Arbor, Mich.

March 11—"Chemical Agents in Battle," MAJOR E. J. ATKISSON, Chemical Warfare Service, Edgewood Arsenal, Md.

April 1—"Fuels," PROF. S. W. PARR, University of Illinois, Urbana, Ill.

April 15—"Motor Fuels Ten Years Hence," PROF. RALPH H. MCKEE, Columbia University, New York, N. Y.

April 29—"Helium, Its History, Properties, and Use in Aeronautics," DR. R. B. MOORE, Chief Chemist, Bureau of Mines, Washington, D. C.

May 13—"The Role Played by Cellulose in the Late War," PROF. HAROLD HIBBERT, Yale University, New Haven, Conn.

Platinum Theft

Attention is called to the fact that on the night of February 6, 1922, platinum to the amount of 100 grams was stolen from the office of F. A. Richmond, Chemical Laboratory, Elmira College, Elmira, N. Y.

Industrial Notes

For the purpose of encouraging research work on glass, the Research Committee of the Glass Division of the American Ceramic Society has made arrangements for providing glass of desired composition and desired form for investigators in this field. The material will be supplied free of charge and no limitations as to the nature of the research will be imposed. The recipients of the material will be under no obligations except that of publication of the results of their investigations, the committee requesting only that wherever possible the *Journal of the American Ceramic Society* be given preference in reporting the results. Inquiries from interested persons may be addressed to one of the following members of the Committee on Research: E. C. Sullivan, Corning Glass Works, Corning, N. Y.; E. W. Washburn, University of Illinois, Urbana, Ill.; R. B. Sosman, Geophysical Laboratory, Washington, D. C.

The statistics for imports of chemicals, drugs, dyes, and medicines for the year 1921 show a decrease in value of 54.8 per cent as compared with 1920. The loss in value for the entire import trade was 52.5 per cent. Receipts of chemical products for recent years are as follows:

1914	$ 88,039,120
1918	151,832,065
1919	126,048,538
1920	211,528,099
1921	85,603,912

In nearly every case the drop from the 1920 figures is due to a general fall in prices, and not to a decrease in volume of imports.

Investment in Chemical Education in the United States, 1920–1921

(Compiled by Research Information Service, National Research Council)

By Clarence J. West and Callie Hull

At the request of the Chemical Foundation of New York City the Research Information Service of the National Research Council has compiled a series of tables showing the investment in chemical education in the United States for the collegiate year 1920–1921. This information was secured by sending questionnaires to the 600 universities and colleges listed in the Educational Directory of the U. S. Bureau of Education. Reports were received from about 450 institutions. This number, therefore, represents approximately three-fourths of all the colleges and universities in the United States. It represents, however, a much larger proportion of the amount of money invested, as practically all of the large colleges and universities responded. In nine states returns were complete; in practically all of the other states returns varied between two-thirds and three-fourths of the institutions listed.

The information was tabulated first by university or college grouped under the individual state, but on account of the length of these tables, the statistics have been summarized by state in Table I. The ten states leading in investment in chemical education for this period are listed in Table II. These figures include not only the actual money invested, but also the appropriations for new buildings and equipment under construction at this time. This latter amount, $7,553,300, is divided between 17 states and 27 institutions. Of these institutions Cornell leads with $2,000,000 and Yale is next with $1,866,900. The sums reported by the other institutions vary between $5000 for Howard College, Alabama, and $465,000 for the University of Minnesota. Twelve institutions reported a total of about $2,000,000 worth of building under consideration.

TABLE II—TEN STATES LEADING IN INVESTMENT IN CHEMICAL EDUCATION, 1920–1921

New York	$ 6,790,015	Minnesota	$ 2,351,210
Massachusetts	4,146,917	Illinois	1,868,983
Ohio	3,196,204	California	1,490,587
Connecticut	2,786,495	Michigan	1,390,850
Pennsylvania	2,404,521	Indiana	1,098,726

Those states having over $500,000 invested in buildings and equipment are shown in Table III. The cost of maintenance and the number of students are also given. From these figures one may roughly approximate the cost per student per year in the states listed.

TABLE III—STATES HAVING OVER $500,000 INVESTED IN BUILDINGS AND EQUIPMENT FOR CHEMISTRY

State	Approximate Valuation of Buildings and Equipment	Cost of Maintenance of Chemical and Chemical Engineering Departments	Total Number of Students
New York	$ 3,973,459	$ 805,556	16,453
Massachusetts	2,793,873	1,345,571	5,954
Ohio	2,014,679	503,825	8,571
Pennsylvania	1,854,852	464,269	6,444
Minnesota	1,515,972	168,447	5,823
Illinois	1,490,272	370,782	7,779
California	1,217,045	271,192	3,869
Michigan	840,499	276,901	4,862
Oklahoma	773,000	88,800	1,786
Indiana	745,000	152,226	3,667
Texas	659,495	204,706	3,393
Connecticut	618,500	151,095	1,351
New Hampshire	605,000	43,500	711
Wisconsin	569,710	236,774	3,361
Missouri	550,105	135,044	2,932
Colorado	546,750	102,462	2,102

TABLE I—INVESTMENT IN CHEMICAL EDUCATION IN THE UNITED STATES, 1920–1921

STATE	Number of Institutions Reporting	Approximate Valuation of Buildings and Equipment	Valuation of New Buildings under Construction and Their Equipment	Funds Received for Chemical Endowment during Year	Cost of Maintenance of Chemical and Chemical Engineering Departments (Salaries, Chemicals, Supplies, Services, etc.)	Total Number of Students in Chemistry (All Courses)		Total Number of Students in Chemical Engineering (where Separate Department Is Maintained)	
						Graduate	Undergraduate	Graduate	Undergraduate
Alabama	8	$ 191,044	$ 5,000	$ 600	$ 39,436	8	901	1	41
Arizona	1	60,000	....	....	17,500	3	250	...	...
Arkansas	5	45,500	....	....	22,000	8	514	...	...
California	12	1,217,045	....	2,350	271,192	44	3,825	14	67
Colorado	8	546,750	....	350	102,462	24	2,078	...	54
Connecticut	5	618,500	2,016,900	....	151,095	47	1,304	...	...
Delaware	1	75,000	....	....	11,682	...	156	...	37
Dist. of Columbia	6	410,233	....	....	121,443	70	1,258	12	133
Florida	3	97,000	....	....	28,450	2	536	...	...
Georgia	8	169,650	....	....	56,543	...	1,255	...	44
Idaho	1	21,000	....	....	18,315	...	291	...	...
Illinois	23	1,490,272	....	7,929	370,782	1,093	6,686	16	342
Indiana	11	745,000	....	201,500	152,226	42	3,625	3	101
Iowa	15	444,210	400,000	....	133,545	19	2,720	2	31
Kansas	14	385,971	82,500	4,000	101,103	44	2,406	...	155
Kentucky	7	100,940	....	75,800	34,929	17	786	...	...
Louisiana	5	374,630	....	....	75,114	23	1,157	5	111
Maine	4	329,679	....	....	49,210	2	563	2	81
Maryland	9	343,489	....	....	97,725	48	1,713	...	...
Massachusetts	16	2,793,873	....	7,473	1,345,571	178	5,776	52	273
Michigan	9	840,499	265,000	8,450	276,901	114	4,748	39	1,435
Minnesota	9	1,515,972	665,000	1,800	168,447	132	5,691	32	132
Mississippi	5	451,000	275,000	22,000	48,650	12	1,165	...	..
Missouri	10	550,105	150,000	1,300	135,044	33	2,899	...	343
Montana	2	220,000	250,000	12,000	28,655	2	400	...	30
Nebraska	8	496,820	50,000	14,000	87,906	13	1,808	...	...
Nevada	1	30,000	....	....	11,800	1	120	...	...
New Hampshire	2	605,000	....	....	43,500	2	709	...	66
New Jersey	3	275,000	....	....	64,309	4	1,028	...	...
New Mexico	3	120,000	....	....	14,600	...	178	...	...
New York	31	3,973,459	2,009,000	2,000	805,556	1,089	15,364	89	744
North Carolina	14	358,000	50,000	2,000	81,300	16	1,690	...	...
North Dakota	4	130,000	....	....	34,258	2	508	...	4
Ohio	31	2,014,679	675,000	2,700	503,825	139	8,432	9	292
Oklahoma	5	773,000	....	....	88,800	10	1,776	...	150
Oregon	5	59,600	....	....	33,423	5	1,047	...	...
Pennsylvania	33	1,854,852	79,900	5,500	464,269	112	6,332	11	257
Rhode Island	2	100,000	450,000	....	36,006	20	833	...	14
South Carolina	11	323,620	....	400	58,780	5	1,141	...	...
South Dakota	6	161,000	....	....	45,276	12	653	...	.
Tennessee	13	450,700	....	....	87,294	60	2,274	...	19
Texas	11	659,495	....	1,000	204,706	36	3,357	6	67
Utah	2	196,093	....	....	20,780	6	714	...	..
Vermont	4	298,675	....	100,000	39,234	2	782	...	.
Virginia	15	436,750	....	52,000	116,501	28	3,101	1	138
Washington	4	263,969	....	....	108,777	18	1,031	...	218
West Virginia	3	43,000	100,000	....	11,750	...	199	...	...
Wisconsin	8	569,710	30,000	716	236,774	98	3,263	8	206
Wyoming	1	....	....	....	6,500	...	85	...	...
TOTAL	417	$28,230,784	$7,553,300	$525,868	$7,739,970	3,643	109,128	302	5,585

SCIENTIFIC SOCIETIES

The Birmingham Meeting

Plans for the Birmingham Meeting, April 4 to 7, are progressing rapidly. Headquarters will be at the Tutwiler Hotel, where the banquet will also be held.

Six special addresses will be given at the General Meeting, including the following:

Van H. Manning, "The Pioneer's Field in Petroleum Research."
Charles L. Reese, "Informational Needs in Science and Technology."
W. C. Geer, "Recent Developments of the Chemistry of Rubber."

Excursions to the steel, by-products, coke, and other industries are planned for Friday and Saturday of the meeting week.

Excursion to Kingsport, Chattanooga, and Muscle Shoals via Special Train to Birmingham

Through a committee, C. L. Parsons, *Chairman*, the Washington Section is arranging for a special train of Pullman cars, leaving Washington at 6 P. M., March 30, spending Friday, March 31, at Kingsport, Tenn., and the Clinchfield region; Saturday, April 1, at Chattanooga; Sunday, April 2, at Muscle Shoals; and reaching Birmingham Monday, April 3.

The train is contingent upon 125 *guaranteed* fares. Early application should be made to secure Pullman accommodations desired.

Tickets should be bought from point of departure, via Washington, traveling over Southern and Norfolk & Western Railroads, direct to Birmingham. If 350 people purchasing tickets by certificate plan are present in Birmingham at the meeting a return ticket *via same route* may be purchased at one-half the regular fare. Extra tickets for side trips and for Pullman accommodations must be purchased in advance and check for same (made out to Charles L. Parsons) must accompany application. No application for space will be considered unless accompanied by remittance.

Extra railroad charges for side trips Johnson City to Kingsport and return and Chattanooga to Muscle Shoals will be $10.87.

Pullman fares all four days:

Upper berth	$13.20
Lower berth	16.50
Drawing room (2 or 3 persons)	58.00

The above charges for Pullman are made to cover necessary guarantees. If Pullman cars are filled, there will be rebate of any excess fare paid. Application for space must be made on or before March 20.

If 125 applications accompanied by full remittance for extra fare and Pullman are not received by that date, the train will be abandoned and all remittances returned. If the train runs, no remittances will be returned for any cause as they are part of the guarantee. Regular straight ticket must be purchased from point of departure and certificate taken to secure reduction on return fare. Special train will be given up at Birmingham and party will return as individuals via Chattanooga, Knoxville, Roanoke, and Lynchburg to Washington, and home. This train is normally open to members north of Washington and east of Pittsburgh as these points ticket south through Washington. Any members living further west who can buy tickets via East Radford, Va., and are willing to return *via same route*, will be gladly received on the train there or at Johnson City, but same extra fare and Pullman rates will apply. Suggestions are being made to western local sections that they arrange for special cars via Muscle Shoals to be attached to train there. These cars cannot be a part of the Kingsport and Chattanooga trip on account of the basic requirement of the railroad that return tickets be sold at a reduced price only over the route for which certificate is issued.

Permission has been obtained to visit the nitrate plant and water power development at Muscle Shoals. *This permission is limited to American citizens and to those who have no personal connection with or financial interest in the manufacture of cyanamide.*

Ladies and personal guests may accompany members.

Detailed plans have not yet been made for the entertainment at Kingsport, Tenn., and at Muscle Shoals, but we have been promised a hospitable reception at both places. Saturday will be spent either at Knoxville or at Chattanooga, probably at the latter city. The region around Kingsport, Tenn., has become an interesting industrial center and large plants, such as the Clinchfield Portland Cement Plant, the extract plant and tannery of the Grant Leather Corporation, a large face brick plant, the wood distillation plant of the Tennessee Eastman Corporation, are in operation. An immense leather working plant of the Simmons Hardware Company and the new plant of the Corning Glass Company are ready for operation, but are at present closed down. The Union Dye and Chemical plant has ceased operations. The plants which are in operation, however, are sufficient to give a very interesting day for members, and it may be possible to extend the trip to South Clinchfield to view the Carbo-coal process of the International Coal Products Company, which is the only going concern making use of processes of low temperature distillation of coal combined with the production of briquetted solid fuel. The possibility of visiting this plant appears to be entirely a question of time. If visited, there will be a slight addition to the railroad fare. At Chattanooga there are important industrial plants, such as by-product coke plants, electric furnace manufacture of ferroalloys, cottonseed and peanut oil refining, hydrogenation of oils, alum plant, etc. Details of the trip are being arranged.

All are familiar with the immense fixed nitrogen development made by the Government at Muscle Shoals, the partly developed water power, and the proposition for the purchase of the same from the Government which is now before Congress. Permission to visit the plants has been granted with the limitation above cited. The people of the immediate locality will arrange a special entertainment for the Society.

Committees

Honorary Chairman: George Gordon Crawford.

Executive Committee: J. F. Carle, Theodore Swan, C. N. Wiley, Max Kuniansky, James T. MacKenzie, J. R. Harris, H. S. Geismer, Alden K. Boor.

Finance Committee: Theodore Swan, *Chairman*, Erskine Ramsey, Frank Miller.

Hotels, Publicity and Meeting Places: C. N. Wiley, *Chairman*, F. G. Cutler, Henry Burn.

Registration and Information: Max Kuniansky, *Chairman*, R. T. Pittman, R. W. Allen.

Banquets: J. T. MacKenzie, *Chairman*, J. H. Adkins, J. W. Moore.

Excursions: J. R. Harris, *Chairman*, Theodore Swan, K. Landgrebe, A. G. Overton, G. St. J. Perrot.

Smokers: Alden K. Boor, *Chairman*, T. S. Bissell, C. W. Hogg.

Transportation: H. S. Geismer, *Chairman*, W. E. Mitchell, R. H. Cunningham.

Ladies' Entertainment: Mrs. Eugenia B. Dabney, *Chairman*.

Papers: Dr. A. C. Montgomery, *Chairman*.

Reports on the Progress of Applied Chemistry

In order that the Annual Reports on the Progress of Applied Chemistry issued by the Society of Chemical Industry may be more widely known in this country, the Society is offering Volume VI (to be published in March) at the reduced price of 10s. post-free, to members of the American Chemical Society. This is the price charged to its own members.

Orders, with remittance, should be sent to Dr. J. P. Longstaff, Journal of the Society of Chemical Industry, Central House, 46 & 47, Finsbury Sq., London, E. C. 2, England.

Calendar of Meetings

American Chemical Society—63rd Meeting, Birmingham, Ala., April 4 to 7, 1922.

American Electrochemical Society—Spring Meeting, Baltimore, Md., April 27 to 29, 1922.

American Institute of Chemical Engineers—14th Semiannual Meeting, Niagara Falls, Ontario, week of June 19, 1922.

American Society for Testing Materials—25th Annual Meeting, Atlantic City, N. J., June 26 to July 1, 1922.

Officers of Local Sections, A. C. S.

The 1922 officers of the New Haven Section are:

President: MILO C. BURT
Vice President: TREAT B. JOHNSON
Treasurer: JOHN L. CHRISTIE
Secretary: BLAIR SAXTON
Councilor: HAROLD HIBBERT

The 1922 officers of the Georgia Section are:

Chairman: C. A. BUTT, Atlanta.
Vice Chairman: Dr. J. F SELLERS, Atlanta.
Secretary-Treasurer: L. B. LOCKHART, 33$^1/_2$ Auburn Ave., Atlanta
Councilor: W. P. HEATH, Atlanta.

American Institute of Chemical Engineers

The American Institute of Chemical Engineers will meet in Niagara Falls, Ontario, at the Hotel Clifton, beginning June 19, 1922. One day will be spent at Buffalo, and one devoted to a boat trip to Toronto with visits to industries there.

The feature of the program will be a symposium on the manufacture of the heavy acids. The Secretary, Dr. J. C. Olsen, Brooklyn Polytechnic Institute, Brooklyn, N. Y., will be glad to correspond with any who may be interested, whether members of the Institute or not.

NOTES AND CORRESPONDENCE

The Outlook in Europe

Editor of the Journal of Industrial and Engineering Chemistry:

It was my privilege to visit England, France, Belgium, and Germany during the months of October and November 1921, and my general impression of the conditions is such that I cannot put my finger on any one particular thing that would restore some of these countries to even a seminormal condition.

BRITISH TARIFF CONDITIONS

England has always been a free trade country, but since the war she has seen her industries slipping, with every indication of going under, and has enacted a general tariff bill, called the "Safeguarding of the Industries Act" in which a duty of 33$^1/_3$ per cent has been placed on all industries which need protection, such as optical glass and optical instruments; scientific glassware; laboratory porcelain; synthetic colors, rare earths, and chemicals. In addition, an Anti-Dumping Act has been enacted, which became a law on October 1, 1921. I can quote only Part 2, Section B, of the Anti-Dumping Act of England, which relates to the depreciation in value of foreign currency, which we would do well to follow:

> Evidence as to price at which similar goods can be profitably manufactured in the United Kingdom.
>
> Evidence to show that the depreciation in relation to sterling of the currency of the country of manufacture is responsible for the fact that the prices at which the goods are sold or offered for sale in the United Kingdom are below the prices at which similar goods can be profitably manufactured in the United Kingdom.

In addition to this, England has protected her dye and synthetic chemical industry by means of embargoes and prohibitions, which prevent some foreign chemicals from coming into the country.

FRANCE AND BELGIUM

The condition in France is still more interesting, for France has enacted a tariff, known as the Law of September 1921, which is composed of four distinct types of tariff. They are known as the "old tariff," "new tariff," "favored nation tariff," and the "coefficient."

The "old tariff" is the one which existed prior to that date, and applies to some materials not made in France, and others not indigenous to France. The "new tariff," generally speaking, is a very high tariff on certain chemicals and manufactured articles. The "favored nations tariff"—from which the United States is conspicuously absent—favors those countries which France has chosen; but the most important and interesting part is the "coefficient." This is a number 2, 3, 4, or more in the fourth column of the Tariff Act, which in every instance is used as a multiple of the duty assessed. In other words, precipitated barium sulfate is assessed at 2 francs per 100 kilos, and includes the coefficient 5; therefore, it is dutiable at 10 francs per 221 lbs.

France has no unemployed men at present; the entire country looks very prosperous.

Belgium is in the same condition, and has a high protective tariff, but I am not in possession of the latest laws on the subject.

THE ECONOMIC CONDITION OF GERMANY

The condition in Germany is exceedingly interesting in view of the fact that by far the largest part of the plants in Germany are working nights. There is no unemployment, as there is no foreign competition. As I pointed out to the Treasury Department last summer (in June 1921), Germany, in addition to her high tariffs, has a list of embargoes which precludes the importation of any material which can be made in Germany out of German raw material. If we wished to retaliate by shipping 1000 tons of barium peroxide to Germany at five cents per ton it could not be done, because the material could not enter any of the customs ports of Germany.

The man who goes to Berlin, lives at a fine hotel, and orders the best wine for a few cents a bottle in our money, and then comes back talking about how prosperous Germany is, is not acquainted with the facts. It is true that Germany is working very hard, and that one passes hundreds of factories brilliantly illuminated at night, particularly in the iron district near Essen, but the workman is being paid in a currency that is continually depreciating, and the savings which he had put aside last year, when the mark was worth 1.6 cents, have depreciated until now their purchasing power is far less than it was a year ago, and their international value has fallen to half a cent. Such a condition is not wholesome, and I feel sure that unless Germany receives a gold loan from the Allies and the United States she may soon find herself in the same deplorable condition as Austria and Poland. Germany is running her railroads at a tremendous loss (approximately thirteen billion marks this year); her post-office shows a deficit of two billion marks, and, while she has neither army nor navy, she is supporting the foreign army on her soil at a cost, equal to, if not greater than, that of France. Another pernicious defect of the financial condition in Germany is the fact that many of her merchants have opened accounts in Holland, England, the United States, and South America, and when they export goods to these countries, they deposit the funds in the gold of that country. The consequence is that raw and manufactured material has been exported, but the money has never been returned to Germany.

Another very depressing effect upon the Germans, particularly in relation to their reparation payments, has been the decision of the Allies in regard to Upper Silesia. It is expected that Germany will pay the indemnity either in gold or in kind, in accordance with Article 175 of the Treaty. It was agreed that Upper Silesia should decide by plebiscite whether it should become a part of Germany or a suzerainty of Poland. The vote was overwhelmingly for Germany, but a little rider at the end of Article 175 states that even if the plebiscite shall decide in favor of one country or the other, the Commission may reverse this decision if they so see fit. It is a long time since I read this particular article and I am not sure I am correct in quoting Article 175, and I know I am not correct as to the exact verbiage used, but such at least was the intent of that paragraph.

I happened to be in Germany at the time that this decision was made, and it had a very depressing effect, not only upon the people but upon the mark; and, while I hold no brief for Germany, my sense of fair play rebelled, for I felt France is encouraging future wars instead of preventing them.

Germany has not the slightest desire for another war, she has not the money, and she has not the men, and, in my opinion, what she wants is to be left alone to work out her own salvation. France would be infinitely better off if she reduced her army of 800,000 men and utilized them for the rebuilding of the devastated zone. Of course, if you go through the battle area as I did from the Ostend coast to Rheims, you feel that no punishment is too great to visit upon Germany, but it is a dangerous thing to allow your passions to get the better of your prudence. Universal peace would not be so far off if the Tammany politicians of France, of which she unfortunately has many, were superseded by safe and sane statesmen.

Mr. Frank A. Vanderlip once stated "You cannot milk a cow and cut its throat at the same time," and that, it strikes me, is what is being done to Germany, in addition to what Germany is doing to herself.

Czechoslovakia ought to be taken for an example, for they are working gladly and peacefully; they have stopped printing money; their internal organization is on a paying basis, and the chances are that that country will come out ahead of all the other Central empires.

As far as stocks of raw materials and finished products in Germany are concerned, Germany will soon come to the end of her tether in the matter of textiles, for, with their depreciating mark, they are unable to buy cotton, wool, and silk at competitive prices. As far as chemicals are concerned, Germany has enough raw material to undersell the world for many years.

MAXIMILIAN TOCH

NEW YORK, N. Y.
December 20, 1921

"The Fire and Explosion Hazards of Commercial Oils"

Editor of the Journal of Industrial and Engineering Chemistry:

In the interest of accuracy, we desire to call attention to a number of errors in the chapter on coal-tar oils in a book by Vlachos entitled "The Fire and Explosion Hazards of Commercial Oils," published by Vlachos & Co., 1921. This book is intended for the enlightenment of fire underwriters. Its object is, therefore, praiseworthy, for underwriters are generally deficient in exact information concerning the complex and highly specialized materials of the oil industries. Unfortunately, the authors themselves do not appear to have exercised sufficient care in presenting the subject of coal-tar oils and this chapter contains a number of statements which can only be described as grossly inaccurate.

Turning to the opening paragraphs of Chapter 16, Page 229, we find the flash point of "about 16° F. below zero" attributed to coal tar. The flash point of crude tar is very difficult to ascertain as the tar always contains considerable moisture and the water vapors practically eliminate any true flash point. It is safe to say that crude coal tar will never flash at temperatures below 180° F. Distilled or dehydrated tars necessarily have the light oils removed during the process of dehydration and the residual tar will flash only at temperatures well above 200° F. The flash point of 16° F. below zero attributed to coal tar by the authors is probably intended to refer to benzene, as will be readily seen by reference to the chapter title and subtitles. Nevertheless, the opening words of the chapter explicitly refer to coal tar as a crude material derived from the by-product coke ovens and gas works.

In the second and third paragraphs of this chapter, the temperature of production of coal tar from coke ovens and gas works is given as 1100° F. and 1500° F., respectively. While carbonization temperatures vary, the temperature in by-product ovens is usually 1800° F., never as low as 1100°, and the temperature in gas retorts is approximately 2000° F. True these temperatures are of no particular significance or interest to the fire underwriters, but if given at all should be stated with some degree of accuracy.

In the next paragraph the authors state that coal tar flashes readily. It does not at ordinary temperatures as expressed above. "When stored in large steel tanks with steel roofs it is an acceptable risk." Steel roofs on coal-tar storage tanks are distinctly unsafe, owing to the corrosive action of the ammoniacal impurities in the liquor which always separates out on the top of coal tar in storage tanks. It is universal practice in the industry to use wooden roofs covered with pitch and felt surfaced with gravel or slag. These roofs will last as long as the tank itself. The steel roofs would not last five years and are always an element of danger by reason of the rapid corrosion. Crude coal tar in storage invariably has a layer of water on top from a few inches to several feet in depth. It is about as free from incidental fire hazard or even conflagration risk as any liquid material could be.

On page 231, we find "the modern coal-tar stills are vertical and the older stills are horizontal." Vertical tar stills are almost unknown in American practice. The horizontal still is standard for discontinuous distillation. This is probably unimportant as direct fired stills are not ordinarily insured. The authors appear to have inspected some very extraordinary installations: *viz.*, continuous stills which are gravity fed; large open tank agitators in which benzene was treated with crude sulfuric acid, etc.

In the last page of this section on benzene, we find the interesting statement that the authors have personally witnessed the violent explosion of creosoted wood and they deplore the use of creosoted wooden floors in "so-called fireproof industrial buildings." In view of the remarkable showing made by creosoted wooden block pavements in the Baltimore conflagration some years ago as compared with the brick and stone pavements, this statement will be regarded with considerable interest by the wood-preserving industry. The explosion of a piece of creosoted wood is unique. The authors should by all means give us the full details concerning this fascinating phenomenon.

We have not read the rest of the book. Doubtless, it may be quite free from the unfortunate errors which we have noticed in the chapter on coal-tar oils, but in turning the pages we did observe what is evidently only a typographical error on page 33 where the boiling point of water is given as 220° F.

Too literal interpretation by fire underwriters of these pronouncements may lead them into some interesting arguments with oil chemists.

S. R. CHURCH

40 RECTOR ST.
NEW YORK, N. Y.
February 6, 1922

The International Trade Situation

The January 7, 1922, issue of *The Chemical Age* (London) contains an interview with Brigadier General Sir William Alexander on the international trade situation, and especially on British industrial problems in relation to those of other nations. Sir William recently made a tour of the United States and Canada, closely concerned with the future of the dyestuffs industry, and is therefore especially well qualified to speak on this problem.

He points out that though the surplus capacity for dyestuff manufacture, for instance, developed during the war may mean a peace-time war of elimination, Great Britain and America have every chance of pulling through since they are uniquely and satisfactorily placed for all the raw materials, if application and determination be added. Britain can maintain her plants in operation provided that British Empire consumers support their own industries, that her chemists and engineers responsible for running plants concentrate toward maximum efficiency, that labor recognize that maximum production per unit of labor or plant is the greatest security for regular and good wages and low cost of living, that the government continue to assist British industries to fight against depreciated currencies and other handicaps to fair trading on equitable terms, and that the government realize that its consuls and trade commissioners overseas should be competent, commercially, to pioneer, advertise and assist in the development of British trade.

The reconstruction of Europe is all-important to Great Britain as an exporting nation, and no opportunity on the part of such solvent countries as Great Britain and America to assist in reconstruction on sound lines to the extent of such finances as can be safely extended should be missed, but the greatest and most enduring assistance will be in the direction of encouraging poor nations to help themselves. Nations whose currencies have fallen so low as to have little or no purchasing values will require to go hungry until they reorganize their internal economies and industries by producing or taking out of the ground the equivalent of currency to balance imports by exports.***** Such a policy is the only permanent and reliable method of stabilizing exchanges.

* * * *

This doctrine carries little encouragement toward a speedy revival of trade in Great Britain, but*****in our present state of reduced circumstances we must not trade beyond our means. *****We shall retrieve our own prosperity more quickly and surely by concentrated development of trade within the Empire, adding such outside business as exhibits a fair commercial risk, rather than retard reconstruction on normal lines by the encouragement of trading with insolvent nations against phantom credits.******

America has recovered from the general depression to a greater degree than any other nation because about 80 per cent of her trade is within her own boundaries, because she has nursed and protected her industries.

* * * *

In the peace-time war for commercial supremacy there will be no room for middlemen. Let us make certain that we do not drift into a position of being neither producers or merchants.

Best interests will be served by a trade recovery that is gradual and not spasmodic. The interregnum of restricted trade should be utilized to the fullest extent in perfecting plant, processes, and production efficiencies for all classes of manufactures for which the country is advantageously placed. Chemicals and dyestuffs, with unlimited sources of coal and coal-tar products, limestone, salt, etc., should form two of the most extensive. When reconstruction and reëstablishment of confidence bring demand we should then be in a position to command a fair share of the world's trade against any fair competition.

* * * *

Consultation between manufacturers and close coöperation between employers and employed should be encouraged to the utmost, with the object of obtaining maximum output, from a minimum of plant, at a minimum cost, and also that we may compete for world trade more collectively as a nation and less as isolated members with no common interests.

The American Potash Industry

Editor of the Journal of Industrial and Engineering Chemistry:

There is a quite justifiable general opinion opposed to a tariff on any material for protective purposes and particularly opposed to any such protective tariff on a material of which the farmers are to a large extent the ultimate consumers. However, the situation as to the tariff on potash proposed in the bill under consideration, in Paragraphs 75 and 1635, is such as to make it actually to the financial interest of consumers to have those paragraphs retained in the tariff bill when finally passed.

Except for the periods from 1915 until 1919, and 1919 to date, the production of potash salts has been a German monopoly because the first developed deposits of soluble potash salts were in Germany and the business was so conducted as to keep it under German control by artificial conditions imposed by the German government.

Prior to 1909 this monopoly had maintained high prices of potash salts, around $38.00 per ton of 80 per cent muriate. In 1909 the German syndicate was broken for a few months and during that time American interests bought potash mines and under the Schmidtman contracts gave those particular mines the large tonnage of the American market, cutting the price to $21.00 per ton of 80 per cent muriate.

With this low price, little more than the cross-country freight on California potash to the eastern United States, the American-owned German mines made the largest profits in their history.

The re-forming of the German syndicate was followed by the famous German 100 per cent export potash tax applied to product of mines which did not belong to the syndicate or which shipped more than half their product out of Germany; this put the American price higher than it was before. The celebrated Hill-Taft settlement followed, putting the price back to $38.00 per ton, and there it stayed until the European war stopped potash coming out of Germany.

Opponents of tariff protection for potash make much of the assertion that, if five years of the sort of embargo that so effectively kept potash out of this country during 1915 to 1919, with the enormous prices that were paid by consumers, did not establish an American potash industry capable of competing with Germany, certainly the protection provided by the paragraphs in the present bill cannot do so and can result only in that much increased cost to the American consumers, the greatest number of whom are the already sadly overburdened farmers.

A careful analysis of the situation, however, will quickly relieve the mind of the erroneous impression thus given by a casual survey.

All the forces of the enormous German potash propaganda had been at work for many years in directing as far as possible all search for American potash to the far western regions from which the freight alone across the country would nearly equal the prices at which Germany could lay down potash on our eastern seaboard, and, as was proved by the Schmidtman contracts above referred to, at an enormous profit to German mines if allowed to operate on large production.

The widespread feldspar and greensand potash deposits of the East were prevented from exploitation by the secret forces of the same propaganda frightening proverbially timid capital away from the enormous investments required in plants and machinery for operation of necessary processes to change this insoluble potash to soluble form.

The hidden deposits of soluble potash that must of necessity exist in the salt fields of the eastern United States could not be accidentally discovered as they had been by hundreds of years of shaft and stope mining for rock salt in the salt fields of Germany, for the very good reason that salt mining in the United States has been entirely developed in the last seventy-five years and confined entirely to the purest veins of sodium salt, where there could not of course be any potash, and this same propaganda exploited to the fullest extent the idea that an all-wise Providence had confined potash deposits to the German salt fields alone.

The European war embargo on German potash therefore found this country totally unprepared to develop quickly any potash production within the limits to which capital could be obtained, except in the salt lakes and deserts of the far West, and only the high prices obtainable justified the costly work of recovery on the comparatively small scale permitted by the limited capital which could be interested. No man who invested a dollar in potash plants during the war period was ever sure of having six months in which to operate without being again subjected to German competition. Consequently investments were made as far as possible with the idea of getting in and getting out quickly with a profit if possible.

After three or four years' record of reasonable profits, some companies actually did get economical operations established, so that with reasonable protection afforded, they can even now produce potash salts at less than double the old German prices.

The exploitation of the several processes for extraction of the insoluble feldspar and greensand potash in the East has gone on slowly and steadily as capital could be secured, and with the protection afforded by the bill in question one plant now almost completed and several more under way will get into operation and will not be hampered by heavy freight from western deposits.

If the present bill had been a law any time before or during the war, American potash production would in less than five years have been on such a scale of magnitude that prices far lower than even the Schmidtman contracts would give handsome profits.

It is a fact well proved by history that whenever American manufacturers are sure of no competition which can have any advantages of foreign cheap labor or foreign government protection, they go into the intensive development of a product on large-scale production with labor-saving mechanical ingenuity that always results in cheapening of that product to a point where foreign competition is left far behind.

With the passage of the bill in question it is a foregone conclusion that capital will be ready and eager to go forward with the developments now so well under way, and in a very short time American quantity production, with the results of the wonderful research work that has been carried out by American chemists for the past five years, will totally destroy Germany's domination of the potash industry of the world. Without this protection, the industry is doomed and German domination will be permanent and complete.

Notwithstanding the fact that the recent German and French potash contracts have been made with American fertilizer companies (three of the principal companies still own large interests in German potash mines), at about the old price ($37.00 per ton of 80 per cent muriate), the price charged the good old American farmer is $52.00 per ton or only a little below the price at which American producers were already offering their American-made potash.

The actual difference to the farmer, therefore, will be but very few dollars and the profit will go to the importer who is sending good American dollars out of this country, instead of to the American mine and factory whose every expense benefits the sadly unemployed ranks of American labor and brains.

H. D. Ruhm

136 Liberty St.
New York, N. Y.
January 20, 1922

Fire at Heyden Chemical Plant

Editor of the Journal of Industrial and Engineering Chemistry:

We have noted in the January issue of the Journal a statement with reference to our fire which is grossly exaggerated.

The plant of the Heyden Chemical Company of America, Inc., Garfield, N. J., was visited by a serious fire on the afternoon of December 12, in the refined salicylic acid section. The fire loss, including use and occupancy insurance, is estimated to be between $550,000 and $600,000.

The conflagration started at 2:45 P. M. in the middle sublimer of a set of three. Two employees were cleaning the hot air chamber. One of them left the chamber and upon returning tripped over a flexible extension cord connected with a properly protected electric light bulb. The lamp fell to the iron grating at the bottom of the hot air chamber, knocking off the guard and breaking the bulb, and the terminal wires came in contact with the iron which caused a short-circuit. The flash ignited the refined salicylic acid in the chamber. The operators endeavored to put out the fire with buckets of water, which failed, and they then closed all dampers, enclosing the flame in the hot air chamber. The sides of the chamber were bulged out by the gas generated from this small fire, which caused the flame to spread instantly to the dust in the room and then to the salicylic acid which had just been removed from the sublimer. The company's fire department had a hose stream playing on the burning sublimer at about the time the dust ignited, which caused a "puff," blowing out the end wall of the building, and the wind carried the flames around the fire protection walls, separating each of the sublimers, and the other sublimers caught fire, causing the destruction of the refined section of the salicylic acid, sodium salicylate and acetylsalicylic acid departments.

The capacity of the destroyed refined salicylic acid section of the plant was approximately 225,000 lbs. of U. S. P. acid per month. The crude equipment is intact.

Of the five men who were burned, four of them have reported back at work and the fifth, the foreman who was most seriously burned, it is expected will be discharged from the hospital early in February. The foreman, who was the most seriously burned, received his injuries through his efforts to turn on the valve controlling the carbon dioxide gas, with which all sublimers were equipped to prevent the possibility of serious fire. He was caught in the "puff" which took place just as he was entering the sublimer room.

F. H. Chamberlain, *President*

Heyden Chemical Company of America, Inc.
Garfield, N. J.
January 18, 1922

The Formula Index

Editor of the Journal of Industrial and Engineering Chemistry:

The work that *Chemical Abstracts* has been doing and is doing for the chemists of America and elsewhere is of the utmost importance. This work has been developing without a backward step from its start in 1907, until just recently. However, the action of the directors of the SOCIETY in stopping work upon the formula index to *Chemical Abstracts* for 1921 is very much to be deplored, as it curtails the usefulness of the journal.

I wish to take this occasion to protest against this action and to ask other chemists interested to file a similar protest. The reasons which lead to my opinion are the following:

The heart of any abstract journal is its index. Chemistry is now so complex that it is utterly impossible to have a simple index. Those responsible for *Chemical Abstracts* realized this and, beginning with the Decennial Index, evolved the most scientific nomenclature yet proposed for such an index. This index is a very excellent one but neither it nor any other complete word index can be used without considerable study and experience with the principles involved.

On the other hand, a formula index especially for organic compounds is extraordinarily simple to use. It furthermore gives more accurate and quicker information as to the presence of a given compound in an index than will a word index.

I trust that some way will be found to restore the formula index to *Chemical Abstracts.* It would be very much better to increase the dues of the SOCIETY or to economize in other directions rather than to drop this formula index. As a matter of fact, a formula index ought to be prepared as a supplement to the Decennial Index, as soon as possible.

R. NORRIS SHREVE

43 FIFTH AVE.
NEW YORK, N. Y.
January 18, 1922

Permanence of the Grignard Reagent

[PRELIMINARY NOTE]

In connection with a series of quantitative studies on the Grignard reagent, particularly the determination of the optimum condition for the formation of this reagent, it was considered desirable to undertake investigations which it is hoped will extend the general usefulness of the reagent, more especially where reasonably large quantities are used.

The Grignard reagent is generally prepared by adding a solution of the appropriate RX compound in absolute ether to magnesium turnings. The RMgX compound so formed is quite sensitive to air, a small amount of moisture, in particular, decomposing a relatively large amount of the reagent. Partly for this reason and the uncertainty concerning its stability, the reagent is very conveniently used directly after preparation. One rarely hears of "stock" Grignard reagent.

It has been found that ethyl magnesium bromide in ether and phenyl magnesium bromide in ether, when protected from the air, are stable after a period of two months. Parallel experiments with ethyl magnesium bromide in the light and in the dark have shown that daylight is without influence on the strength of the solution. The investigation is being extended to a variety of typical RMgX compounds, some in highly concentrated ethereal solutions, over a longer time period.

A study is also being made of pastes, of so-called "individual" compounds, and of solvents other than ether, with the intention of decreasing the fire hazard and the comparatively large expense attendant on the use of ether as a medium.

HENRY GILMAN
CHARLES H. MEYERS

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE, AMES, IOWA
December 23, 1921

Contamination by Aluminium in Analytical Work

Editor of the Journal of Industrial and Engineering Chemistry:

Considerable trouble has been met in the courses in qualitative analysis at the University of Illinois on account of the appearance of decidedly appreciable amounts of aluminium during the course of the procedure. It was found to come from two rather unexpected sources.

One source was the filter papers used. These papers were purchased for the usual "qualitative" grade, and behaved very satisfactorily so far as holding fine precipitates was concerned. Upon filtering acid solutions, however, enough aluminium was leached out to give decided tests for this element. Sulfates and traces of iron were also detected. Quantitative examination showed that, as an average of several determinations, a 10-cm. paper contained 3 mg. of aluminium and iron (computed as Al_2O_3 and Fe_2O_3), to say nothing of considerable amounts of acid-soluble silica. The source of this contamination can only be conjectured. The presence of the aluminium and sulfate suggested alum, which might have come by the use for filter stock of trimmings from paper mills and binderies, which would contain alum as sizing. The acid-soluble silica, on the other hand, indicates clay, which is sometimes used as a filler for "weighting" paper.

A second source of aluminium was found in the porcelain evaporating dishes used. Digesting acid solutions in the brand of dish which has been used in this laboratory for the past two or three years results in the solution of various amounts of aluminium and silica, particularly if the glaze has been broken by previous use. It was found that more than 50 per cent of the dishes in the student cupboards would show a mark if a graphite pencil were drawn across their interior surfaces. As an extreme example, one badly pitted dish lost 6.9 mg. upon boiling $6\ N$ HCl in it for 15 min. As a substitute for these dishes, the classes in qualitative analysis have been using small beakers, which approximate the familiar "Pyrex" cooking vessels in composition. These were found very satisfactory, and it may be interesting to note that the indications are that the breakage accounts of the students will be reduced somewhat by their use.

These experiences are passed along to the rest of the chemical brotherhood "for the good of the order."

J. H. REEDY

CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
November 16, 1921

Holland's Tariff Situation

Editor of the Journal of Industrial and Engineering Chemistry:

In reading Mr. Watson Davis' interesting article on conditions in Europe [THIS JOURNAL, **14** (1922), 73], I note certain somewhat erroneous statements.

It is true, as Mr. Davis states, that Switzerland and Holland, as neutral border states, have to face severe competition. What Switzerland may have done to overcome this drawback I do not know, but so far Holland has not "raised stringent tariff barriers to prevent a flood of goods from Germany, Austria, and other low-wage-plane countries." Many people in Holland are of the opinion that only such a barrier, in the form of a protective tariff bill, can save our trade and industry from gradual economic starvation. It is not my intention to discuss this question here, but simply to call attention to a misunderstanding of our condition. In my opinion, Holland's economic breakdown as a consequence of Germany's industrial and financial policy toward her is not a mere phantom, but a real fact.

H. BAUCKE

KONING & BIENFAIT
DA COSTAKADE 104, AMSTERDAM, HOLLAND
January 19, 1922

Ramsay Memorial Fellowship

The Trustees of the Ramsay Memorial Fund have requested the National Research Council to nominate a Fellow to devote his whole time to research in chemistry in some English university upon a stipend of 250 pounds sterling per year, with an additional allowance of 50 pounds for apparatus. The National Research Council has appointed a nominating committee consisting of F. G. Cottrell, Chairman of the Division of Chemistry and Chemical Technology, National Research Council, Washington, D. C.; E. B. Mathews, Chairman of the Division of Geology and Geography, National Research Council, Washington, D. C., and Professor of Mineralogy and Petrography, Johns Hopkins University, Baltimore, Md.; and W. E. Tisdale, Secretary of the Division of Physical Sciences, National Research Council, Washington, D. C.

This Committee is willing to receive applications from any American chemists who have taken a degree with distinction in chemistry in a university or college within the United States, and who are now connected with a university or college, or have recently been graduated therefrom.

The appointment will be for the academic year 1922–1923. Under the general regulations of the Ramsay Memorial Fund, Fellows are eligible for reappointment.

Applicants should furnish:

1—Certificates or other satisfactory evidence of birth, health, character, and academic or other distinctions.

2—A written application stating:

(*a*) Education and employment to date, and particularly the nature, extent, and place or places of his academic studies and research.

(*b*) Particulars of the work and place of work proposed; and

(*c*) The names and addresses of not more than three references well acquainted (one or other of them) with the health, character, capacity, and career of the applicant, without, however, any written testimonials from them or others. One of the references should be a teacher under whom the candidate has studied, or a high official of his university, college, or other place of education.

These Fellowships are open in chemistry, either pure or applied, and work may be carried on at any university, college, or other place of higher education, or an industrial laboratory within the British Empire. Their object in this instance has, in addition to the stimulation of research, the special earnest wish on the part of English scientists to cultivate the wider acquaintance and good fellowship which is so much to be desired between scientific men of the world.

The Ramsay Memorial Fund for research in chemistry within the British Empire was founded in 1920 to commemorate the services to chemistry of Professor Sir William Ramsay, K.C.B., F.R.S., with an initial endowment of £14,000. Since that time several special endowments have established additions to this Fund, and special Fellowships with appropriate regulations are granted under: The Glasgow Special Fund; Royal Hellenic Government Special Fund; Federal Government of Switzerland and of Swiss Subscribers Special Fund; Royal Italian Government Fund; Fund of the Honorary Advisory Council for Scientific and Industrial Research, Canada; Royal Swedish Government Special Fund.

Applications should be mailed before April 15 to W. E. Tisdale, Secretary, 1701 Massachusetts Ave., Washington, D. C.

American-Made Chemicals

Editor of the Journal of Industrial and Engineering Chemistry:

We have received recently from two large American universities requests for quotations on chemicals in which the description of the chemicals with comments on them is *written in German*, in several cases chemicals of German origin being specified which are available from American sources in the United States.

It is, of course, not likely that an American university supported by American funds and whose students hope eventually to find positions in the American chemical industries would really intend to exclude American-made chemicals and to accept only chemicals of foreign origin.

From the manufacturer's point of view, however, it is important that orders be in English because the naming of chemicals in German might prevent a supply house from supplying American chemicals, even though they had the latter in stock and would prefer to quote on them under other conditions.

I venture to suggest that when such documents are received written in German from American sources they be sent back with a request that they be translated into English.

C. E. K. MEES

EASTMAN KODAK CO.
ROCHESTER, N. Y.
January 26, 1922

Protecting Metallic Laboratory Hardware and Utensils from Corrosion

Editor of the Journal of Industrial and Engineering Chemistry:

In most laboratories there are acid fumes and in all there are metal burners, ring-stands, tripods, and similar tools. This means that unless much pains are taken there is often considerable trouble from corrosion. The writer has found that to sand-blast and paraffin-dip all such utensils effectively preserves them even from the fumes of strong acids in hoods and enclosed places. The objection to enamel baked on such tools is that it chips off and exposes the metal, but the rough surface holds the softer paraffin in place in spite of much handling. Incidentally this method is quite inexpensive. A steel vise so treated and in daily use for over two years shows little or no corrosion in a laboratory where there are acid fumes continually.

W. G. BULLARD

CHEMICAL LABORATORY
UNITED SHOE MACHINERY CO.
BEVERLY, MASS.
December 6, 1921

An Experimental Study of the Significance of "Lignin" Color Reactions
(Correction)

In my paper of the above title, published in THIS JOURNAL, **13** (1921), 625, the following errors on page 626 escaped correction:

Column 1, 4th line from bottom, "light transmission" should read "light absorption."

Column 2, line 2, "bands of highest transmission (minima of absorption)" should read "bands of absorption."

Column 2, line 4, "11.30 for safrol" should be "13.35 for safrol."

Column 2, line 5, "minimum" should read "maximum."

Column 2, line 8, "minima" should read "maxima."

ERNEST C. CROCKER

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
January 9, 1922

A Revision of the Optical Method for Analyzing Mixtures of Sucrose and Raffinose
(Correction)

Three typographical errors are to be noted in the paper by C. A. Browne and C. A. Gamble [THIS JOURNAL, **13** (1921), 793].

On page 795, Formulas 11 and 13 and the formula for N should contain plus signs instead of multiplication signs.

WASHINGTON NOTES

Muscle Shoals

On February 2 the Secretary of War sent the Henry Ford Muscle Shoals offer to Congress, accompanied by his report and appended documents, which included a detailed analysis of the offer by the Chief of Engineers and by the Chief of Ordnance, and on February 6 he transmitted similar data to the Senate. The House referred the matter to the Committee on Military Affairs and that committee started its public hearings on February 8, the Secretary of War being the first witness to appear before the committee. He stated that he preferred a 50-year lease but that he was perfectly willing to waive this personal preference if the committee preferred the 100-year period. He did not understand that the production of nitrates by Mr. Ford at Nitrate Plant No. 2 would be sufficient in amount to affect the market throughout the whole country, as he estimated Mr. Ford's output would not be more than one-thirtieth or one-fortieth of all of the fertilizer used in the country. He felt that while there was no reason whatever to doubt Mr. Ford's sincerity, there was nothing in the agreement to prevent his successors from abandoning the operation of the plant if they saw fit and hence he thought that there should be some guarantee in the contract that the lessee would continue to manufacture nitrates and fertilizers and suggested that this might best be accomplished by the formation of a company so that the contract would be with the company rather than with Mr. Ford personally.

Major General Williams, Chief of Ordnance, followed the Secretary of War and occupied the greater part of one day's sessions in explaining valuations of properties involved in the Ford offer. He stated that it had cost the Government about $88,000,000 to construct Nitrate Plants Nos. 1 and 2, the steam power plant at Muscle Shoals, the Waco Lime Quarry, and the Gorgas Warrior plant and the transmission lines. The present value of these plants he estimated at $16,000,000 and their scrap value at $8,000,000.

Major General Lansing H. Beach, Chief of Army Engineers, was then called before the committee. He said there are certain features in the 100-year lease which should receive consideration because of the slowness in the development in the market for power in that locality. He also felt that another feature of the award to Mr. Ford which deserved consideration was the fact that the Tennessee River possesses an immense potentiality with regard to water power development. He stated that there is no stream in the country, considering the amount of water which it carries and the steepness of its slope, which will furnish the amount of water power that the Tennessee River does, except perhaps the St. Lawrence.

Colonel Hull, Acting Judge Advocate General, was the next witness and answered questions relative to the legal aspect of the Ford proposal.

Mr. Ford did not appear before the committee, but was represented by Mr. W. B. Mayo, engineer, who stated that Mr. Ford was not willing to modify his proposal in any way except to clarify the language and that he would not consider a 50-year proposal. It is his plan to use Nitrate Plant No. 1 to make the raw materials that go into the manufacture of automobiles and Nitrate Plant No. 2 for the manufacture of fertilizers. He further intends to use all the power developed at the various Muscle Shoals plants for his own purposes.

The Senate has referred the Ford proposal to the Committee of Agriculture and Forestry, and the committee will hold its first public hearings on February 16. The proponents of the Ford measure feel that their cause is in the hands of friends with this committee and those opposed to the Ford proposal feel that they will be well taken care of in the House Committee on Military Affairs.

The Dye Probe

The subcommittee of the Judiciary, appointed to investigate the dye and chemical industry, has been completed with Senator Shortridge of California as chairman. The other members of the committee are Senator Reed of Missouri and Senator Ernst of Kentucky. The support of chemical manufacturers throughout the country has been pledged to the committee by Dr. Chas. H. Herty in his capacity as President of the Synthetic Organic Chemical Manufacturers Association, and R. C. Jeffcott, President of the American Dyes Institute, has written to the committee offering to coöperate with them and facilitate their labors in every way. The public hearings began February 20.

Patent Office Relief

On February 14 the Senate passed, without amendment, the Patent Office relief bill. It begins to look as if the bill will become a law before This Journal issues and that a measure of relief is in sight for the Patent Office which now has on hand 62,000 applications for patents aside from 6000 applications for trademarks and designs—more work than was received in that office for any entire year up to 1909 and enough work to keep the Patent Office busy if it closed its doors and did not do any new work for the rest of the year.

Standardization of Glassware

At the request of the Section of Physics and Chemistry of the Association of Scientific Apparatus Makers of the United States of America, the Bureau of Standards called a conference of manufacturers of chemical glassware and representatives of users and dealers to consider the standardization of sizes and shapes of beakers, flasks, and other lines of apparatus. The conference opened at the Bureau of Standards at 10 o'clock on January 28 and later adjourned to the Shoreham Hotel.

The manufacturers expressed a willingness to coöperate in the unification and standardization of sizes and shapes along the lines of the recommendations of the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society which have previously been published in This Journal, **13** (1921), 1070, and a subcommittee was appointed by the conference to work out the details of this standardization. The working committee consists of representatives of the Corning Glass Works, the Kimble Glass Co., the Vineland Flint Glass Co., and Whitall Tatum. Mr. Walter Eimer was authorized to serve as executive officer.

Metric System Referendum

At a meeting of the National Council of the Chamber of Commerce of the United States on the afternoon of February 9, at the Washington Hotel, Washington, D. C., the question "Shall there be legislation for the compulsory adoption of the metric system?" was discussed. The report to the Board of Directors by the Special Committee on the Metric System was read by Mr. Edmund D. Fisher, chairman of the committee. This report favored the taking of a referendum throughout the country on the question of the adoption of the metric system, and suggested the wording of the question substantially in accord with the Ladd bill now before Congress. After addresses on the advantages of the metric system by Howard Richards, Jr., Secretary of the American Metric Association, and on the disadvantages of the system by W. C. Wilson, Assistant to the President of the American Institute of Weights and Measures, a lively discussion took place during the course of which both sides were presented in detail. At the close of the discussion, the Council passed a resolution recommending the postponement of the referendum to a more fitting time.

Recovery of Potash Lost in Washing Wool

A small wool washer made for recovering potash from fleeces in a solution of sufficient concentration to make the recovery of the potash profitable has been designed and is being tried out by the Bureau of Chemistry. It is said that the average fleece contains about 4 per cent of potash by weight, but in the ordinary method of washing wool it comes out in such dilute solution that it does not pay to recover the salt.

About 600,000,000 lbs. of wool are scoured in the United States each year, and if only 3 per cent of potash are recovered it would amount to 18,000,000 lbs. of actual potash that would be available for use in fertilizers. Some nitrogen is also recovered from wool along with the potash.

The United States Tariff Commission has expanded its census of dyes and coal-tar chemicals to include other synthetic organic chemicals. The prompt return of the schedules by the manufacturers it is hoped will insure earlier publication of the census than has heretofore been possible.

The National Agricultural Conference which assembled in Washington at the call of Secretary of Agriculture Wallace adjourned on January 28 after adopting a resolution favoring the acceptance of the Henry Ford offer for Muscle Shoals.

February 14, 1922

LONDON LETTER

By Stephen Miall, 157 Haverstock Hill, N. W. 3, Hampstead, England

I have heard no regrets that the year 1921 has now come to a close. It has been the worst year for chemical industry in history. There may have been in the middle ages worse years from the point of view of the progress and well-being of mankind, but in those early days applied chemistry, as such, did not exist.

We seem here—it may be a delusion—but we seem to have passed the worst of the depression. The textile industries are a little better than they were, the engineering industries are no worse; they hardly could be. The home markets are on the whole not quite so stagnant as they were six months ago, and the export business seems to be a little brighter. Of the manufacturers of chemicals, no large firm has gone into liquidation, and of the merchants very few. The soap industry seems now to be blessed by a number of orders and in some other branches of industry the outlook is brighter. No reasonable man here expects good trade in 1922 but almost all think it will be better than during the last few months. The political horizon has undoubtedly cleared even in Europe, where fears and animosities dating back a few centuries are apt to flare up at intervals because some sentiment of nationality or something equally unsubstantial has been aroused. It happens that this continent is at the moment fairly peaceably inclined and it is quite possible that in the course of the current year some of the old antagonisms will die down. It is, of course, hopeless to expect the Prussians to be friendly with the French or the Turks with the Greeks, but we may get to the stage where they can do business together.

Sometimes in the English papers we read of developments in applied chemistry but when they are closely investigated they turn out to be waiting for further capital or something of that sort. This is the fate of the Claude process for synthetic ammonia here and of other means of getting rich beyond the dreams of avarice.

I have after a good deal of search come across one development actually in being—not an epoch-making one, certainly, but of interest for all that—an improved method of making sodium silicate. Instead of dissolving the lumps of crude sodium silicate obtained by roasting together soda-ash and sand, and then evaporating the aqueous solution to a sirup, the new method introduces into a ball-mill a limited quantity of water and the lumps of crude silicate, which are ground up together until a mass is obtained which sets to a solid on cooling and contains 75 per cent of silicate. The new process is operating on a considerable scale in South Yorkshire and is said to be successful. The owners of the works claim a very considerable saving by eliminating the usual dissolving and evaporation. Probably the process with some modifications is capable of being adapted to other varieties of manufacture.

Those engaged in low-temperature carbonization of coal continue to speak with confidence of the satisfactory working of the plant at Barnsley, and they promise to disclose some new features a month or two hence. If these claims are well founded I hope to visit the works again and to give a detailed description of the novel features.

January 9, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

PATENT REFORM

French inventors are under the law of 1844 in the matter of industrial ownership. This legislation has been recognized as superannuated for a long time, and a campaign for its reform is now being conducted. The chemists, who are the inventors most frequently involved, are specially active in this campaign.

For instance, a scientific communication made by the Académie des Sciences or in one of the chemical societies becomes public property, by this very fact, especially if a patent has not been taken out at the same time. Furthermore, it may happen that a scientific communication may not contain patentable material, though it may possess the highest technical interest; it does not always constitute a novelty, but frequently it may involve a condition of reaction which may lead to a great industrial improvement. Also, certain chemists take out patents but do not immediately find manufacturers and financiers to make possible their development; patent fees are paid for some years; then the chemist becomes discouraged and stops these payments. Some time later he is surprised to see his patents and processes put into operation.

All these gaps would need to be filled by creating what the *Syndicat des Inventeurs*, who are at the head of the movement, call *"le droit de suite,"* a right which would obviously be limited to a certain period, fifty years, for example. There would be an almost complete fusion between this *droit* and what we French call *"le droit d'auteur."* Scientific treatises would be deposited, just as models or machines, and to this depot the *droit d'auteur* would be paid by the concessionaire.

Chemists differ on the question of how to know whether or not a new compound should be patented, and after a long discussion at the Congress of Industrial Chemistry it was decided that a new chemical compound could be patented as a new industrial product, but that the holder of the patent would be obliged to grant a license to any inventor who found a better method of preparation for this product. The conditions of this license would be settled by agreement of those interested or fixed by the authorities.

Further, the vote was passed that patents of chemical products could be expropriated by the State for public use.

PROPOSED RESEARCH COUNCIL

The French Senate is now considering a first draft of a law organizing an "Office national des recherches scientifiques, industrielles et agricoles." This organization is modeled on the National Research Council in the United States.

This plan has been fought from the first by Parliament, who see in it a duplication of the laboratories of the big teaching establishments of the state. It has been decided that the part of the new office would be one of coördination between the different laboratories, not only of the state but also of private industry. There have been established in France some laboratories analogous to the Mellon Institute, and these organizations would coöperate in the work of this office.

AMERICAN DEGREES FOR SALE

An ill-worded announcement which appeared in a French chemical paper has disturbed a number of our American friends. Individuals without authority have been offering to secure advanced degrees in American universities upon payment of a sum of money. I, who have seen many of your universities and laboratories, know that a degree can be obtained only by serious research work. The activity of the numerous American chemical societies and their many publications are still further witnesses that students at the universities are forwarding science and that the diplomas are the fruit of their labor. It is no less true that many French chemists have received from America circulars offering to secure these diplomas.

In France, we are publishing notices discrediting this, but it would also be well if the foreign ambassadors of the United States would publish an advertisement in order to avoid such attempted trickery in the future.

January 8, 1922

OBITUARIES

Charles Baskerville

Charles Baskerville, chemist, cultured gentleman, and loyal friend, died of pneumonia on the night of January 28 at his home in New York City. For nearly four weeks he had fought a brave but losing fight for his life. The news of his death has brought sadness and a deep sense of personal loss to his friends in many states of the Union and to those outside its bounds who had learned to esteem him and to value his friendship. The mere outline of his life and scientific achievements can tell but part of the story to those who knew him best and were nearest to him.

Underwood & Underwood

CHARLES BASKERVILLE

Dr. Charles Baskerville was born in Mississippi June 18, 1870. Entering the University of Mississippi at sixteen years of age, he completed two years of academic study there. Later he spent a year at Vanderbilt University and further pursued his studies at the University of Virginia, devoting himself especially to the study of chemistry under Mallet. In 1891, he came to the University of North Carolina as part-time assistant in chemistry and, on completing the requirements, in 1894 received the Ph.D. degree. While on leave of absence for part of 1893 he studied under Hofmann at the University of Berlin.

During the fourteen years of his connection with the University of North Carolina he advanced from assistant to assistant professor, associate professor, professor, and, from 1900 to 1904, head of the department of chemistry. He proved himself an able teacher and kept in close touch with his students, showing a keen and sympathetic interest in all that concerned them, especially in their athletic sports where he acted as adviser and friend.

From the beginning of his graduate career he entered with zealous energy upon scientific investigation. His special interest lay in the field of the rare earths and many articles were contributed by him to the Society's *Journal*.

He became a member of the American Chemical Society in 1894 and later, as councilor and chairman of important committees, rendered much valuable service. He was one of the most constant attendants upon the annual meetings, effectively laboring for the best interests of the Society. He was also a Fellow of the London Chemical Society; a member of the Society of Chemical Industry; of the American Electrochemical Society; of the New York Academy of Sciences; of the Franklin Institute; and of the American Association for the Advancement of Science.

In 1904 he became professor of chemistry and director of the laboratory at the College of the City of New York, designing and supervising the erection of the new laboratory. His interest in research continued, tending more and more to the technical or applied side of chemistry, and this at last practically occupied his attention. In this connection may be mentioned his work on anesthetics, fats, oils, paper recovery, and other important matters. Several books have been published by him, including a text for schools, several for college classes, an account of the investigations upon the radioactive substances, and a volume on anesthetics.

This necessarily brief outline reveals but little of the indomitable energy of the man, his multifarious activities, and the fine service rendered to the communities of which he was at any time a member. Bright, cheery, with most attractive personal characteristics and gifted in many ways, he will be greatly missed and his memory will be kept fresh by his many associates and friends.

F. P. VENABLE

William Frear

In the early morning hours of January 7, 1922, William Frear died from an apoplectic stroke, suddenly, at his home in State College, Pa. Chemistry lost an indefatigable worker, one of the pioneers of the science as applied to agriculture, in general, and to food production and legal regulation, in particular. His associates lost a zealous and inspiring co-worker, a patient thinker, a prudent counselor, and a true friend.

He was born March 24, 1860, at Reading, Pa., the son of the Rev. George Frear and Malvina (Rowland) Frear. After preparation in the public schools, he studied at Bucknell University (B.A. 1881), Harvard University, and Illinois Wesleyan University (Ph.D. 1883).

WILLIAM FREAR

On completion of these studies, Dr. Frear immediately entered the government service under the newly appointed Chief Chemist, Dr. H. W. Wiley. In 1885, he received the appointment of Assistant Professor of Agricultural Chemistry at the Pennsylvania State College where he was soon recognized as a leader in his subject, both in the College and in the State Experiment Station. He maintained, however, official and active association with the Federal service, doing notable pioneer work in the formative period of the enactment of Food and Drug laws, both State and Federal. As fundamental to and preparatory for this legislation, the Committee on Food Standards was appointed. As chairman of this Committee, it was Dr. Frear's duty to conduct a voluminous correspondence, make extensive literature searches, hold hearings at which antagonistic interests were in action, sift the evidence judicially, and draw a conclusion. The industry, care, thought, and tact which he displayed in this work is probably known only to the very few who were closely associated with him. The point of view and method of the scientific investigator is also too generally overlooked in this work. His services were again called for when in 1914 there was established the Joint Committee on Definitions and Standards, of which he was chairman at the time of his death.

As a true pioneer in agricultural college teaching and experiment station work, the scope of his interest and of his scientific production was wide, including meteorology, lime production and use, tobacco culture, soiling crops, composition of foods and feeds, including forage plants, laws to control the production and sale of fertilizers, foods and drugs, and kindred subjects.

The list of scientific societies of which he was a member and the positions of honor and responsibility, which he held in these societies and in his official life, testify to a life of remarkable breadth and high endeavor.

His social and civic activities were equally broad, keeping him engaged continually for his family, his neighbor, his church, his town, his state, and his country. He well fulfilled the specification of Phillips Brooks for a "four-square man."

Isaac King Phelps

Personals

Charles A. Roos, president of the firm of Charles A. Roos, Inc., 429 East 91st Street, New York, N. Y., manufacturers of copper chemical equipment, died suddenly of heart disease on the afternoon of Wednesday, January 11, 1922, in the New York Athletic Club, of which he had been a member for more than twenty years. Mr. Roos collapsed just as he was about to enter the water of the swimming pool.

Mr. Roos, who was sixty-three years old, was born in New York and was widely known through his various business interests. His firm not only manufactured much of the copper chemical equipment used in synthetic organic chemical manufacturing plants around New York City, but also produced a large amount of the copper equipment used by the large breweries in this vicinity. It is understood that the business will be carried on under the direction of his son, Mr. Charles A. Roos, Jr., who has been general manager of the concern for some years.

Frank R. Eldred, for many years chief chemist and director of the scientific division of Eli Lilly & Co., and **Frederick C. Atkinson,** chemical director of the American Hominy Co., manufacturers of cereal products, vegetable oils, sugars, and sirups, have organized the firm of Eldred and Atkinson, consulting chemists and engineers, with offices at 48 East 41st St., New York City, and 1857 Gent Ave., Indianapolis. Mr. Eldred will have charge of the New York office while Mr. Atkinson will remain in Indianapolis.

Mr. W. S. Frisbie recently resigned his position as Chief of the Bureau of Food, Drugs and Oil, State Department of Agriculture of Nebraska, to accept an appointment as Chemist in Charge of the Office of Coöperation, Bureau of Chemistry, Washington, D. C.

Mr. Jerome Alexander has recovered from his lengthy illness and has become president of the Uniform Adhesive Co., Inc., Brooklyn, N. Y., manufacturers of glues, gums, pastes, and adhesives.

Mr. Ernest W. Dean of the Bureau of Mines Experiment Station, Pittsburgh, Pa., has resigned from the Bureau, and is now with The Standard Oil Company of New Jersey.

Dr. Paul E. Klopsteg, formerly with the Leeds & Northrup Co., Philadelphia, Pa., is now with the Central Scientific Co., Chicago, Ill.

Mr. John P. Harris, chemical engineer for the Allbright-Nell Co., formerly of New York, is now located at 829 New York Life Building, Kansas City, where he will represent the Allbright-Nell Company in the southwest.

Dr. W. W. Skinner, Assistant Chief of the Bureau of Chemistry, has been elected chairman of the Joint Committee on Definitions and Standards to succeed Dr. William Frear, deceased.

Mr. E. M. Bailey, Agricultural Experiment Station, New Haven, Conn., has been appointed as the representative of the Association of Official Agricultural Chemists on this committee to fill the vacancy caused by the death of Dr. Frear.

Mr. John Helfrich, who for the past four years served as manager of the Information Bureau of the Chemical Catalog Co., Inc., and who was in charge of the Service Department of This Journal, has resigned to establish an office at the Chemists' Club Building, New York City, as a consulting chemist specializing in the development of products that find an application in the leather industry. Prior to his association with the Chemical Catalog Co., Mr. Helfrich was engaged in the leather industry as chemist and assistant plant superintendent.

Industrials

The Bethlehem Laboratories, Inc., a $5,000,000 corporation, has been organized in Pittsburgh to manufacture a new antiseptic, known as hyclorite, which is said to possess 175 times the germicidal strength of hydrogen peroxide. Among the incorporators are Homer D. Williams, president, Carnegie Steel Co.; Taylor Allerdice, vice president, National Tube Co.; and Dr. J. J. Reilly, U S. Shipping Board. The plans of the corporation include the construction of a modern chemical plant in Pittsburgh.

At the annual meeting of the stockholders of Monsanto Chemical Works, the following directors were elected: John F. Queeny, Gaston DuBois, Edgar M. Queeny, Theodore Rassieur, H. O. McDonough, J. D. Lumaghi, and J. R. Goodall. The following officers have been elected for the year 1922: John F. Queeny, chairman of the board; Gaston DuBois, president; H. O. McDonough, vice president; W. R. Phemister, treasurer; Edgar M. Queeny, secretary; C. A. Zacher, assistant secretary.

The Commonwealth Edison Company of Chicago has opened a new $10,000,000 power plant, which when completed will generate 250,000 h. p. It is planned later to build another 250,000 h.-p. station on the shores of Lake Michigan at Waukegan, which will fit into a scheme of electric superpower development of Wisconsin, Illinois, and Indiana. The Chicago system has become the hub of a network of interconnected electric transmission lines in the upper Mississippi Valley which spreads nearly to Minneapolis on the north, southwest to the Mississippi River, and south to the coal fields of Kentucky.

The Drug and Chemical Section of the New York Board of Trade and Transportation has elected Frank C. Starr, Sharp & Dohme, chairman; August Wasserschied, Mallinckrodt Chemical Works, vice chairman; William A. Hamann, Roessler & Hasslacher Chemical Co., treasurer; William F. McConnell, secretary; Clement C. Speiden, Innis Speiden & Co., representative of the Section in the Board of Trade and Transportation.

E. L. Pierce, president of the Solvay Process Co., Syracuse, N. Y., has resigned, and will be succeeded by E. D. Winkworth, president and executive vice president of the Semet-Solvay Company. Mr. Pierce has also resigned his position as vice president and director of the Allied Chemical and Dye Corporation.

The Dyestuff Department of E. I. du Pont de Nemours & Co., Inc., has recently been reorganized with a view to the better handling of the technical and commercial problems of the industry. F. W. Pickard, vice president, has been relieved of his duties on the executive committee to become general manager, with W. F. Harrington as assistant. C. A. Meade, vice president and former general manager, and M. R. Poucher, former director of sales, have been made executive staff officials. Both are directors of the company. Cesare Protto, formerly assistant to Mr. Poucher, has been made director of sales.

The Combustion Engineering Corporation has opened a branch office at 806 First National Bank Building, Pittsburgh, Pa., in charge of Mr. W. C. Stripe, formerly manager of the Philadelphia office.

The National Aniline & Chemical Co., Inc., has announced the production of two new dyes, National wool green S and National quinoline yellow.

The Argentine Army has just placed its first order for American ammunition with E. I. du Pont de Nemours & Co. Previously a large part of the army's ammunition was purchased through German concerns.

BOOK REVIEWS

The Vitamins. By H. C. Sherman, Professor of Food Chemistry, Columbia University, and S. L. Smith, Specialist in Biological and Food Chemistry, U. S. Department of Agriculture. American Chemical Society Monograph Series. 260 pp. Book Department, The Chemical Catalog Company, Inc., New York, 1922. Price, $4.25.

Barely a decade has elapsed since the word "vitamin" was originated; yet to-day it is found not only in contributions to scientific journals but also in the pages of the popular magazines and newspapers and on the billboards by the highways. After all, it is not utterly surprising that the vitamins have become something to conjure with. Anyone who has actually followed the demonstrations of the unique physiologic potencies of these hitherto unidentified factors in nutrition—substances which promote well-being not by furnishing energy in measurable calories or foodstuffs in grams but rather by contributing some "little item" in food that spells nutritive success—can better appreciate the unanticipated significance of their discovery.

Quite naturally there has been and still is much confusion and misunderstanding about vitamins, what they are, where they occur, and how they function. Most contributions to science that lend themselves readily to popular exposition experience a similar history. There is at present an insistent demand for information that shall not be merely guesswork or superficial compilation. The intelligent interpretation of a scientific subject still in the making, yet already comprising results recorded in a thousand or more contributions to technical journals, requires an expert who is more than a mere abstractor. It is, indeed, fortunate that Professor Sherman and his colleague, experienced in the investigation of vitamins and related aspects of nutrition, have undertaken the timely task of preparing this monograph for the American Chemical Society's series. The contribution is comprehensive without being too diffuse. It reviews the history of the subject, the properties and distribution of the three now recognized specific vitamins, their relation to certain "deficiency diseases," and the place of vitamins in the problem of the food supply. The review of the successive discoveries which led to the development of the vitamin hypothesis is singularly accurate and intelligently discriminating. In this respect it quite surpasses in quality most of the stuff which has been purveyed as history of an interesting phase of scientific progress. In fact, the book gives the impression of first-hand information on every page. Here is a volume from which the nontechnical reader can derive instruction in readable form regarding the occurrence of vitamins in foods and their significance in nutrition, and "make possible an intelligent use of food so as to provide adequately for our vitamin needs along with our other nutritional requirement, and without going beyond the range of our ordinary staple articles of food." The trained investigator, on the other hand, will find the limitations of knowledge undisguised and the unsolved problems for research brought to his attention by the critical form of the review.

The elaborate bibliography itself guarantees that the new monograph will become the vade mecum of the rapidly growing numbers of persons who are curious, scientifically or otherwise, about vitamins.

Lafayette B. Mendel

The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions. 190 pp. Published by His Majesty's Stationery Office, London, 1921. Price, 2s. 6d. net.

A prefatory note by the Department of Scientific and Industrial Research upon whose advice this pamphlet was published, says:

> In view of the growing industrial importance of colloidal physics and chemistry and with the intention of surveying critically the present state of knowledge as an aid to future development, the Councils of the Faraday Society and the Physical Society arranged a joint Conference on the subject which was held on the 25th of Oct. 1920........It must be understood that in these circumstances the Department of Scientific and Industrial Research accepts no responsibility for the statements of opinion or fact contained in this report.

The remark and the discussion following each section are indicative of the fact that there is not yet complete unanimity of opinion on many points of colloid chemistry. The science is in a state of flux, of constant criticism, experiment, and search for further light; it has the vitality of youth and growth.

Many well-known names are included among those who presented papers or took part in the discussion. Following an introductory survey by Svedberg is a paper on the general structure of colloids by W. Pauli. Then follow papers on *Emulsions and Emulsification* by Donnan, Clayton and Bhatnagar; on *The Physical Properties of Elastic Gels* by Hatschek, H. R. Proctor, Bradford, Barratt and Zsigmondy; on *Glass and Pyrosols* by Sir H. Jackson and M. W. Travers; on *Nonaqueous Colloidal Systems* by Sir Robert Robertson (nitrocellulose), Barr and Bircumshaw (cellulose acetate), F. Sproxton, B. D. Porritt (rubber), and Wolfgang Ostwald; on *Precipitation of the Disperse Systems*, by Willows, J. N. Mukherjee, W. Harrison, Wm. Clayton, Chatterji and Dhar, A. G. Lowndes (lead azide), and W. E. Hughes (electrodeposition of metals); on *Electric Endosmosis and Cataphoresis* by A. W. Porter, W. R. Ormandy, and H. Freundlich.

Appendix I is Jacques Loeb's paper on "The Proteins and Colloid Chemistry" (familiar to readers of *Science* and the *Journal of General Physiology*), where the author concludes that the behavior of the proteins contradicts the idea that the chemistry of colloids differs from the chemistry of crystalloids—though long before Graham's time, and surely ever since, it has been recognized that certain wide differences exist between the two.

Appendix II is a very valuable and interesting Inaugural Dissertation by H. Kneebone Tompkins, which since 1896 had lain unpublished at the University of London. Much important and time-saving work is undoubtedly thus buried in oubliettes. While Tompkins' work dealt mostly with rubber, he drew some very interesting analogies between vulcanized caoutchouc and other substances, notably metals, *which he regarded as colloids.*

Although many of the papers presented had already been published in the journals of the societies, and also in the *Kolloid Zeitschrift*, the Committee is to be thanked for rendering them all accessible in one volume, with discussion. This pamphlet will be in the library of chemists interested in colloids, and will arouse the interest of those who are not. Chemists cannot be like the Bourbons, who "learn nothing and forget nothing." Research demolishes old ideas so rapidly that often our textbooks are teaching theories and even "facts" which are recognized as erroneous.

Jerome Alexander

The Fire and Explosion Hazards of Commercial Oils.[1] By William Vlachos and C. A. Vlachos. xvii + 292 pp. Copyright by Vlachos & Co., 1921. Price, $5.00.

This book relates primarily to the fire hazard of the animal, vegetable, and mineral oils of commerce, together with the commercial processes of their manufacture and refining. The common solvents used for extracting oils are included. Essential oils are not referred to. There are chapters relating to hydrogenation, sulfonation, vulcanization, nitration, fuel oil burning systems, casinghead gasoline plants, ethyl and wood alcohol, and fire causes in the petroleum industry. In addition an oil schedule is presented which includes flashing points, iodine values, volatility, and what is referred to as the "fermentation value." Numerical values representing the comparative fire hazard are assigned to the oils and solvents of which there are fifty-five. This rating is referred to as the "Vlachos Grading."

The subject matter presented is based largely on the experience of Vlachos & Co., Philadelphia Inspectors, and on available technical literature. The field covered in the limited space of the book is too large to include much detail, and the information given is general in character, but the more important hazards are not neglected. The subjects are treated in a nontechnical manner and in a free conversational style from the standpoint of the underwriters' practical inspector. The book is of value to the inspector, the busy underwriter, and the chemist or chemical engineer requiring information on the above phase of the subject rather than on the chemical phases or the chemical and physical fundamentals involved.

The first eight chapters on animal and vegetable oils appear to represent the best part of the book. The chapters on sulfonation, vulcanization, and nitration appear to be too brief. The Vlachos Grading is similar in form to Underwriters' Laboratories classification of the hazardous properties of liquids, (better known as the National Fire Protection Association method), except that in the Vlachos Grading the iodine value is employed. In the opinion of the reviewer it would have been of assistance to the reader to include a brief reference to and comparison of the Vlachos Grading with other methods of classification of hazards. It is also thought that a bibliography referring to the technical literature on the subject would add to the value of the book.

A. H. Nuckolls

Contemporary Science. By Benjamin Harrow. 17 x 11 cm. 253 pp. Boni and Liveright, New York, 1921. Price, $0.95 net.

The subdivisions are: Introduction, by Benjamin Harrow; Modern Physics, by R. A. Millikan; The Structure of Atoms and Its Bearing on Chemical Valence, by Irving Langmuir; Engineering before and after the War, by Sir Charles Parsons; Methods of Gas Warfare, by S. J. M. Auld; What Are Enzymes, by Benjamin Harrow; Natural Death and the Duration of Life, by Jacques Loeb; The Physiology of the Aviator, by Yandell Henderson; Twenty-five Years of Bacteriology, by Simon Flexner; Before and after Lister, by W. W. Keen; The Measurement and Utilization of Brain Power in the Army, by R. M. Yerkes; Conceptions and Misconceptions in Psychoanalysis, by Trigant Burrow; Einstein's Law of Gravitation, by J. S. Ames.

Millikan cites the following as the ten most important advances in physics of the last twenty years: the verification of the atomic and kinetic theories; the divisibility of the atom; radioactivity; the atomicity of electricity; the electrical origin of mass; the nucleus atom; the nature of X-rays; crystal structure; the atomic numbers; the quantum relations.

Langmuir discusses the octet theory and concludes that:

> In the past the term valence has been used to cover what we may now recognize as three different types of valence, as follows:
>
> 1—Positive valence: the number of electrons an atom can give up.
> 2—Negative valence: the number of electrons an atom can take up.
> 3—Covalence: the number of pairs of electrons which an atom can share with its neighbors.
>
> It is recommended that only for valences of the covalence type should definite bonds be indicated in chemical formulas. One of the particular advantages of the present theory is that it becomes easy to distinguish between covalence and the other types, and thus to predict with certainty in what way electrolytic dissociation will occur, if at all.

Sir Charles Parsons lists the development of aircraft and of sound ranging and listening devices as the two big engineering achievements during the war and the development of the steam turbine and of electrical distribution as the pre-war achievements. Col. Auld's paper on gas warfare is already familiar to the chemists. Harrow advocates the view that an enzyme is a salt in the broad sense adsorbed by a colloidal complex which is usually protein-like. Loeb finds that the life of aseptic fruit flies doubles approximately for ten degrees drop in temperature, which suggests to him that life is a chemical reaction and that death occurs normally when the reaction is finished. If man could live at all with the temperature of his blood at 7.5° his average life would be about nineteen hundred years.

Henderson points out that life is often compared to a flame but that a candle is affected by the proportions of oxygen and nitrogen while man depends solely on the absolute amount of oxygen. Flexner shows that antitoxins are effective against diseases from toxalbumins, etc., but not against the more numerous diseases involving microbes which have penetrated deeply into the organs. Dr. Keen gives the almost incredible percentage of deaths after amputations owing to infection in the days before Lister. Going to a large hospital for an operation in those days was practically equivalent to a death sentence.

Wilder D. Bancroft

Technical Records of Explosives Supply, 1915-1918. III. Sulfuric Acid Concentration. 91 pp., 30 illustrations. 12s. **IV. The Theory and Practice of Acid Mixing.** 93 pp., 25 illustrations. 12s. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1920. 19 x 28 cm. each.

Before the war the Kessler system was regarded in Europe as the most successful type of concentration plant for spent sulfuric acid, an unavoidable by-product in all nitration processes, though the Cascade system had long been used in this country. As, after entrance into the war, the English found it impossible to get delivery of Kessler plant, the Cascade system was adopted on a large scale because it admitted more readily of rapid improvization from accessible material than any other, but the higher temperatures required for the greater concentrations caused such volatilization of the sulfuric acid as to compel the covering in of the lower basins of the cascade and the aspiration of the fumes through coke scrubbers. As soon as possible, therefore, Gaillard and Gilchrist concentration plants were erected and Cottrell precipitation plants installed.

Volume III of this series is devoted to the description and consideration of these three types of plants. Under each section there are given, with detailed plans, a description of the plant and its method of operation, and the general principles governing its construction and operation, but one is most impressed by the extent of the data based on experience that are presented. Thus some 24 pages are given to illustrating in detail how the heat balance for the gas producers and Gaillard towers was ascertained, the object stated being "to estimate the thermal efficiency of the gas producers and to allocate all the thermal losses," and, in recording the method of solution of the problem, there is given a description of the means by which the experimental data were obtained. The truly practical character of this publication is emphasized by the paragraphs on "starting up a unit" and "shutting down a unit" of the Gaillard plant, for technical writers too often omit such essential information.

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[1] See letter by S. R. Church, p. 240, of this issue.—Editor.

Volume IV deals, in Section I, with "acid cycles, acid balances, and control of plant output," the several classes of acid cycles dealt with being TNT, nitroglycerin, and guncotton and nitrocellulose, since each of these products requires for its manufacture a special "mix" and yields a characteristic "spent." Section II deals with "the position of the acid mixing plant in the acids cycle, and the procedure adopted in mixing," and seven pages are assigned to "the calculation of mixes" and thirteen to "the calculation of dopes," while graphs with which to facilitate the operations are given. Section III deals with "plant and process for acid mixing" in some 34 pages and, while necessarily descriptive, it contains many pages of illustrative calculations and several tables of data. Here as elsewhere, one is impressed by the careful accounting for energy as well as for matter.

What has been said of Volumes I and II of this series[1] holds true for the volumes now under consideration. Typographical errors are very uncommon and those observed are of little importance. These volumes should be especially valued by the teacher who seeks concrete examples for his pupils, for they are to be found here in great abundance, while the student will find in this record from practice convincing evidence of the importance of this method of accounting.

CHARLES E. MUNROE

The Riddle of the Rhine. By VICTOR LEFEBURE. 279 pp. W. Collins Sons & Co. Ltd. Glasgow, Melbourne, Auckland; London, 48 Pall Mall, 1921. Price, 10s, 6d.

The importance of gas warfare, again emphasized by international consideration of reduced armaments, justifies the increasing literature of this field. The "Riddle of the Rhine" is a candid authoritative discussion of the subject from the standpoint of the English nation. Major Lefebure is a chemist, a veteran of two years at the front, and former liaison officer between England and France. He was a member of several interallied technical and supply organizations and after the Armistice played an important part in the official allied inspection of German chemical factories, and in bringing vital chemical data before his country. His broad qualifications for authorship in this field are evidenced in his scientific, military, and philosophical presentation, and in the fairness and justice with which he appraises the contributions of the several allied countries. France's quick success and courageous struggle for early production of yperite, her development of a bromine industry in Tunis under wartime handicap, America's overwhelming activities and great research organization, "second only to the I. G.," all are carefully accredited. The struggle for initiative, the strategic role of production in chemical warfare, the evolution of weapons through cloud attack, artillery shell, solid toxic substances, and finally mustard gas, which defied complete protective measures, are accurately analyzed and illumined by specific history. Germany's conceded lead in this mode of warfare was due to a flexibility in research and production, inherent in her varied chemical resources. These gave surprise possibilities, the essence of successful war. The allies lacked quick means of converting research ideas into casualties.

To Major Lefebure, the riddle of the Rhine is the ominous, impenetrable potentialities of the I. G. bristling the Rhine and its tributaries. "It has added economic cohesion to technical efficiency, and is to-day the largest technically efficient potential instrument of war in the world." The author avowedly believes in chemical disarmament of Germany, and points to the failures and difficulties in enforcing the Treaty of Versailles in chemical matters. The inherent difficulties in the inspection by a League under agreements to refrain in times of peace from chemical preparedness are searchingly presented. In fact, the logical end of the author's argument is a world balance of chemical power, either through competitive militarism, industrially disguised, or agreed ratios.

We had suspected that the war and the press had exhausted all the imaginary possibilities of future chemical weapons, but we are still able to react with interest to the author's suggestion of future armies staggering to their fate because of a change in the viscosity, through exposure to the desired chemical, of the liquid contents of the semicircular canals of the inner ear, thus destroying the sense of equilibrium!

The book is written by a man who knows and feels, and has the gift of utterance. It is peculiarly in line with American convictions on the subject and stirs the reader with the tremendous difficulties and weaknesses of current internationalism built along pre-1914 lines.

W. LEE LEWIS

Coke-Oven and By-product Works Chemistry. By THOS. BIDDULPH-SMITH. Cloth 6 x 9, x + 180 pp., 62 illustrations and 7 folding plates. Charles Griffin & Co., Ltd., London; J. B. Lippincott Co., Philadelphia, 1921. Price $7.00.

This book is essentially one of laboratory methods for use by chemists at by-product coke-oven plants and gas works; especially the former, for it does not cover the subject of photometry and gas purification. It gives methods for testing coal and coke, gas, flue gases, tar, pitch, ammonia, and benzene products. Several other tests which are frequently required in the above industries are given, and one chapter has been devoted to calorimetry and pyrometry.

The chapter on coal and coke includes methods for sampling and gives a method for testing the coking property of coal, but methods for ultimate analysis, porosity, and shatter tests are omitted.

The book is particularly useful at benzene recovery and refining plants. Thirteen graphs give boiling temperatures for any mixture of two oils, such as carbon bisulfide, benzene, toluene, and xylene. Other graphs show the relation of the specific gravity of benzene to carbon bisulfide and paraffin content and thus enable the benzene plant chemist to make a quick estimation of the carbon bisulfide or paraffin content.

The book comprises methods which are in general more familiar to the gas and coke-oven chemists of Europe than to those of America. The principles involved are essentially the same, except for modifications which American chemists have applied. It is not a serious objection that the work is based on English practice since it is almost imperative that our chemists should become familiar with the experience and practice of other chemists before they can judge the relative merits of various methods and their applications to individual problems.

A few examples of the differences between the methods given in this work and those of American practice are as follows: In the analysis of coal and coke the sample is ground to pass a 30-mesh sieve, not a 60-mesh sieve as in American practice. In the analysis of gas, oxygen is determined first, whereas in America oxygen is determined after the illuminants. In the distillation of benzenes a standard Engler flask is used, whereas in American practice a standard 200-cc. side-neck flask of slightly different dimensions has been adopted. In the refining of benzenes the acid wash test is judged by the color of the acid layer, apparently without comparison with standard colors, as is done in American practice.

The methods which are given are of a standard nature and generally those which have been accepted as reliable. The work is comprehensive, and the methods are stated as briefly as possible.

E. F. BLACKIE

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[1] THIS JOURNAL, 13 (1921), 1176.

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

January

The possibility of using the by-products of sugar making, especially the heavy molasses residue, for the production of **alcohol** as a **motor fuel** has only recently attracted general attention in Cuba. The current price for motor spirit as sold to the consumer is 27 to 30 cents, as compared with gasoline at about 45 cents, and while it does not appear probable that Cuban alcohol can give serious competition to gasoline outside the island, it is made from materials which, in many seasons, sell at very low prices, and its use appeals to local patriotism. (Pp. 24–5)

Statistics are given relative to the production of **mineral oil** in the Dutch East Indies during the calendar years 1917, 1918, 1919 and 1920. (P. 26)

A demonstration was recently given of the new type of **oil-fuel burner,** known as the "Reid-Erskine liquid fuel atomizer and burner." Among the advantages claimed for it are the high efficiency it possesses, due to the complete atomization of the liquid fuel, and the transformation of the atomized fuel into a light inflammable gas, thereby producing complete combustion. (P. 27)

Experiments have recently been conducted in Norway on the production of coal from **cellulose lye.** A factory has been erected which it is claimed will produce 8000 tons of coal from lye that was formerly dumped in the run as waste. (P. 31)

A decided decrease in British trade in **naval stores** during the first 10 months of 1921, as compared with the corresponding periods of 1913 and 1920, is reported. (P. 33)

The total French production of **naval stores** for 1921 is estimated at 31,000 tons of turpentine and 105,000 tons of rosin, pitch, etc., or 4000 tons less turpentine and 15,000 tons less rosin than in 1920. (P. 34)

Nysaland has revised its **import duties** on kerosene, petrol, motor spirits, and lubricating oils. (P. 47)

Western Samoa has established new import and export duties on **copra.** (P. 47)

The export restriction on **petroleum** products from Tunis has been removed. (P. 48)

The Italian government has announced a 30 per cent reduction in the fixed price for **lime citrate.** (P. 54)

German exports of **heavy chemicals** showed a decline, by volume, during November as compared with October of 12.0 per cent and of dyes of 3.0 per cent. (P. 57)

Statistics are given relative to the production of the **zinc** and **lead** mines of Algeria during 1920. (P. 65)

The **oil** industry in Russia under Bolshevik régime is described. (Pp. 87–9)

Recent developments in the Tampico **oil** fields show that the 25,000-bbl. well of heavy oil in the San Geronimo district contains oil of heavy gravity, testing around 14° Bé., or more like Panuco crude. It is the lowest gravity oil found between Panuco and the southern extremity of the south fields. (Pp. 89–90)

A change has been made in the Australian **import duty** on arsenate of lead, and import duties have been deferred until March 31, 1922, on carbonate and bicarbonate of soda and soda silicate; soda ash; caustic soda; and citric acid. (P. 99)

A market for **cement** is reported to exist in Guatemala. (P. 110)

Attention is called to the value as a **tanning material** of the plant *Acacia arabica,* which French experiments have shown can be used for tanning either alone or with sumac, quebracho, and oak bark. It would appear that it might replace Sicilian sumac, of which 7000 tons were imported into France in 1913. (P. 142)

Under the new Denmark Emergency Tariff Law increased duties are levied on **acetic acid.** (P. 156)

A Brazilian decree continues the American **preferential duties** for 1922 on paints and colors, cement, and varnish. (P. 157)

A French import duty of 2.50 francs per 100 kilos will be applied on **benzene** intended for motors and for fuels. (P. 157)

The Italian customs authorities have been instructed to permit the unrestricted exportation of **potassium salts.** (P. 157)

German production of **nitrogen** by **atmospheric fixation** is reviewed and the statement made that calcium cyanamide factories in Germany have an output now of approximately 500,000 tons, with a nitrogen content of about 100,000 tons. (Pp. 164–5)

The new statistical classification for **petroleum** and its products exported from the United States, which became effective January 1, 1922, is given. (P. 194)

The production of **crude oil** in Rumania is reviewed. (Pp. 194–5)

The **wolfram** mines at Hatch's Creek, Northern Territory, Australia, which, during the war, furnished 50 per cent of the wolfram marketed throughout the world, have been abandoned because of the fall of the market and the high costs of production. (Pp. 200–1)

The **import duty** imposed by Salvador upon chlorides of lime and calcium has been removed. (P. 212)

Beginning with the January number, the Monthly Summary of Foreign Commerce issued by the Statistical Division of the Bureau of Foreign and Domestic Commerce will present export figures for **chemical glassware.** Quantities as well as values will be given. (P. 255)

Exports of **crude petroleum** from the United States during December 1921 showed a decrease of approximately 40 per cent from the November figure. Comparative statistics are given of petroleum exports for the past three years, the 1921 exports showing a decrease over 1920 but an increase over 1919. The imports of petroleum for December showed an increase, as did also the total imports for 1921, the total 1921 imports increasing about 800,000 gal. over the 1920 imports and more than doubling the amount imported during 1919. (Pp. 267–8)

A translation is given, in part, of an address on the present status of the **petroleum** question in Argentina. (Pp. 268–9)

The production of **petroleum** in Argentine during 1921 showed a considerable increase over the 1920 production. (P. 270)

Peru has relaxed its control on the exportation of **cottonseed.** (P. 281)

An increase in the **import duty** on gasoline is proposed in Brazil and changes have been made in the duties on mineral oils and residues, paraffin candles, and calcium carbide. (P. 281)

France has increased her **import duties** on lubricating **oils,** heavy oils, and residues of petroleum and other mineral oils. (P. 281)

France has changed her **import duties** on **fixed oils** (cottonseed oil, sesame, and peanut oils) for the manufacture of alimentary fats. (P. 281)

A little-known source of **copra** is being developed in the former German possession in New Guinea. (P. 294)

The Japanese law and regulations relating to the **camphor** oil monopoly, with all amendments to 1910, is on file in the Far East Division of the Bureau of Foreign and Domestic Commerce. (P. 294)

The **mining laws** and regulations of China, which were last promulgated by the Chinese Government on March 11, 1914, are available in circular form upon application to the Bureau of Foreign and Domestic Commerce. (P. 294)

A copy of the translation of the June 21, 1915, Japanese law for the encouragement of the manufacture of **dyes** and **drugs** may be secured by addressing the Bureau of Foreign and Domestic Commerce. (P. 294)

STATISTICS OF EXPORTS TO THE UNITED STATES

Peru—(P. 18)	Bordeaux—(P. 34)	Brazil—(P. 128)
Vanadium	Rosin	Rubber

CURRENT PUBLICATIONS

NEW BOOKS

Aggregation and Flow of Solids. Sir G. Beilby. 256 pp. Price, 20s net. Macmillan & Co., Ltd., London.

Colloids: The Formation of Colloids. The. Svedberg. 127 pp. Illustrated. Price, $3.00. D. Van Nostrand Co., New York.

Conductivity: Further Light on the Theory of the Conductivity of Solutions. Guy Clinton. 15 pp. Price, 50 cents. Chemical Publishing Co., Easton, Pa.

Construction Cost Keeping and Management. Halbert P. Gillette and Richard T. Dana. 572 pp. 264 illustrations. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Dairy Chemistry: A Practical Handbook for Dairy Chemists and Others Having Control at Dairies. Henry Droop Richmond. 490 pp. Illustrated. Price, $6.00. J. B. Lippincott Co., Philadelphia.

Dietetics: A Laboratory Handbook for Dietetics. Mary Schwartz Rose. Revised edition. 156 pp. Price, $2.10. The Macmillan Co., New York.

Drug Industry: The Brown Book: Credit Guide and Reference Book, Published for the Drug, Chemical and Allied Lines throughout the United States. Drug and Chemical Credit Association. 1500 pp. Price, $50.00 net. Drug and Chemical Credit Association, New York.

Dyes: Matières Colorantes Artificielles: Leur Fabrication et leur Emploi. H. Vassart. Preface by J. Garçon. 233 pp. Price, paper, 30 fr. Albin Michel, Paris.

Edible Fats and Oils, Their Composition, Manufacture and Analysis. W. H. Simmons and C. Ainsworth Mitchell. 2nd revised and enlarged edition. 192 pp. Price 11s. Scott, Greenwood & Son, London.

Electrons and Ether Waves. Sir William Bragg. 23rd Robert Boyle Lecture. 14 pp. Price, 45 cents. Oxford University Press, New York.

Elements of Fractional Distillation. Clark Shove Robinson. International Chemical Series. 204 pp. Illustrated. Price, $2.50 net. McGraw-Hill Book Co., Inc., New York.

EMF Electrical Year Book: A Combined Dictionary, Encyclopedia and Trade Directory of the Electrical Industry. Frank H. Bernhard, Editor. 1000 pp. Price, $10.00. D. Van Nostrand Co., New York.

Equations: First Course in the Theory of Equations. Leonard Eugene Dickson. 168 pp. 26 figures. Price, $1.75 net. John Wiley & Sons, Inc., New York.

Fuel Research Board: Second Memorandum on Fuel for Motor Transport. Department of Scientific and Industrial Research. Price, 6d. H. M. Stationery Office, London.

Gas Cylinders: First Report of the Gas Cylinders Research Committee. Department of Scientific and Industrial Research. Price, 7s. 6d. H. M. Stationery Office, London.

Handbook of Laboratory Glass-Blowing. Bernard D. Bolas. 106 pp. Illustrated. Price, $1.50. E. P. Dutton & Co., New York.

Hydroelectrical Engineering: A Book for Hydraulic and Electrical Engineers, Students and Others Interested in the Development of Hydroelectric Power Systems. Richard Muller. 431 pp. Illustrated. Price, $6.00. G. E. Stechert & Co., New York.

Metallurgy of Zinc and Cadmium. H. O. Hofman. 340 pp. Illustrated. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

The Microscope. Conrad Beck. 144 pp. Price, 2s. 6d. R. & J. Beck, Ltd., London.

Microscope, Its Design, Construction and Application. F. S. Spiers, Editor. 260 pp. Illustrated. Price, $5.50. J. B. Lippincott Co., Philadelphia.

Mineralogy: A Textbook of Mineralogy. Edward S. Dana and William E. Ford. 3rd edition, revised and enlarged. 720 pp. 1050 figures. Price, $5.00 net. John Wiley & Sons, Inc., New York.

Organic Chemistry: Fundamental Principles of Organic Chemistry. Chas. Moureu. Translated from 6th French edition by W. T. K. Braunholtz. 399 pp. Price, 12s. 6d. net. G. Bell & Sons, Ltd., London.

Perfumes, Essential Oils and Fruit Essences Used for Soap and Other Toilet Articles: A Concise and Practical Account, Including Their Chief Constants, Methods of Analysis, and Numerous Practical Recipes, for the Chief Perfuming Mixtures. Geoffrey Martin. 145 pp. Illustrated. Price, $3.50. D. Van Nostrand Co., New York.

Physics: Essentials of Physics. George Arthur Hoadley. Revised edition. 544 pp. Illustrated. Price, $1.60. American Book Co., New York.

Precious Metals: Les Métaux Précieux. Jean Voisin. 264 pp. Illustrated. Price, 35 fr. J.-B. Baillière et Fils, Paris.

Qualitative Chemical Analysis: A Systematic Qualitative Chemical Analysis: A Theoretical and Practical Study of Analytical Reactions of the More Common Ions of Inorganic Substances. George W. Sears. 199 pp. 4 figures. Price, $1.75 net. John Wiley & Sons, Inc., New York.

Rare Elements: An Introduction to the Analytical Chemistry of the Rarer Elements. 64 pp. Price, $1.25. Author and Publisher, Louis J. Curtman, College of the City of New York.

Sewerage and Sewage Disposal—A Textbook. Leonard Metcalf and Harrison P. Eddy. 598 pp. 220 illustrations. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Sewerage and Sewage Treatment. H. E. Babbitt. 531 pp. 186 figures. Price, $5.00 net. John Wiley & Sons, Inc., New York.

Soaps: A Practical Manual on the Manufacture of Domestic, Toilet, and Other Soaps. George H. Hurst. 3rd revised and enlarged edition. 432 pp. 92 illustrations. Price, 21s. net. Scott, Greenwood & Son, London.

Synthetic Tannins: Their Synthesis, Industrial Production and Application. Georg Grasser. Translated by F. G. A. Enna. 143 pp. Price, 12s. Crosby Lockwood & Son, London.

Thermodynamics, Abridged. William D. Ennis. 2nd edition, corrected. 244 pp. 73 illustrations. Price, $4.00. D. Van Nostrand Co., New York.

Works Chemistry: Der Betriebs-Chemiker: Ein Hilfsbuch für die Praxis des Chemischen Fabrikbetriebes. Richard Dierbach and Bruno Waeser. 3rd edition. 334 pp. Illustrated. Julius Springer, Berlin.

Vitamins. H. C. Sherman and S. L. Smith. American Chemical Society Monograph. 270 pp. Price, $4.25. Chemical Catalog Co., Inc., New York.

RECENT JOURNAL ARTICLES

Ammonia: La Saponificazione Ammoniacale e la Fabbricazione Industriale dell' Ammoniaca. Felice Garelli. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 11, pp. 487–89.

Artificial Musk: Le Musc Artificiel. E. Noelting. *Chimie et Industrie*, Vol. 6 (1921), No. 6, pp. 719–36.

Clay: The Microscopic Examination of the Mineral Constituents of Some American Clays. H. G. Schurecht. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 1, pp. 3–24.

Colloidal State in Metals and Alloys. I—Molten Metal. II—Crystallization. III—White Metal and Brass. IV—Iron and Steel. Jerome Alexander. *Chemical and Metallurgical Engineering*, Vol. 26 (1922), No. 2, pp. 54–58; No. 3, pp. 119–23; No. 4, pp. 170–72; No. 5, pp. 201–07.

Colloids: The Influence of the Concentration of Colloids on Their Precipitation by Electrolytes. Harry B. Weiser and Henry O. Nicholas. *Journal of Physical Chemistry*, Vol. 25 (1921), No. 9, pp. 742–57.

Copper Refining: Calculation of Anode-Furnace Charges in a Copper Refinery. C. M. Brister, Jr. *Engineering and Mining Journal*, Vol. 113 (1921), No. 4, pp. 167–69.

Dyeing of Acetyl Silk. J. F. Briggs. *Canadian Dyer and Color User*, Vol. 2 (1922), No. 1, pp. 5–8.

Dyes: Differential Reduction of Vat Dyes. Wallace J. Murray. *American Dyestuff Reporter*, Vol. 10 (1922), No. 1, pp. 17–20.

Dyes: The Employment of a New Group of Naphthalene Intermediates in the Production of Azo- and Disazo-Dyes. Gilbert T. Morgan and Hugh Gilmour. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 1, pp. 3*t*–6*t*.

Earthenware Bodies and Glazes. H. H. Sortwell. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 12, pp. 990–98.

Electrolytic Corrosion of Lead-Thallium Alloys. Colin G. Fink and Charles H. Eldridge. *Brass World*, Vol. 18 (1922), No. 1, pp. 19–21.

Explosives and Fertilizers. Alfred H. White. *Chemical and Metallurgical Engineering*, Vol. 26 (1922), No. 4, pp. 161–65.

Hydrogénation de quelques Huiles d'Animaux Marins. Henri Marcelet. *Chimie et Industrie*, Vol. 6 (1921), No. 6, pp. 765–68.

Isotopes: Notes on Some Recent Chemical Theories: Isotopes. Stephen Miall. *Chemical Age* (London), Vol. 6 (1922), No. 136, pp. 66–68.

Leather: Anthrax Prophylaxis in the Leather Industry. Alfred Seymour-Jones. *Journal of the American Leather Chemists Association*, Vol. 17 (1922) No. 2, pp. 55–65.

Lubrication and Lubricants. Leonard Archbutt. *Journal of the Society of Chemical Industry*, Vol. **40** (1921), No. 24, pp. 287*t*–93*t*.

Magnesium: Some Recent Applications of Magnesium in Synthetic Organic Chemistry. Harry Hepworth. *Journal of the Society of Chemical Industry*, Vol. **41** (1922), No. 1, pp. 7*t*–11*t*.

Microscope: Some Applications of the Microscope in Research. Henry Leffmann. *Journal of the Franklin Institute*, Vol. **193** (1922), No. 1, pp. 81–88.

Paint: Special Paint Vehicles and Varnishes. E. W. Storey. *Paint, Oil and Chemical Review*, Vol. **73** (1922), No. 4, pp. 10–12, 28.

Research: Finding the Better Way: How Scientific Research Aids Modern Industry. Charles E. Ruby. *Industrial Management*, Vol. **62** (1921), No. 5, pp. 303–08; No. 6, pp. 375–78; Vol. **63** (1922), No. 1, pp. 26–29.

Synthetic Tannins and Their Uses in Leather Manufacture. G. F. Knowles. *Journal of the Society of Leather Trades' Chemists*, Vol. **6** (1922), No. 1, pp. 19–23.

Textiles: The Utilization of X-Rays in the Examination of Textiles. Reginald Truesdale and C. Hayes. *Textile Colorist*, Vol. **44** (1922), No. 517, pp. 35–38; *The India-Rubber Journal*, Vol. **62** (1921), No. 27, pp. 1099–1102. Reprinted from *The Journal of the Textile Institute*, Vol. **12** (1921), No. 11.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Coal and Coke Mixtures as Water-Gas Generator Fuel. W. W. Odell. Illinois Coal Mining Investigations Coöperative Agreement. (This paper was prepared under a coöperative agreement with the Illinois State Geological Survey and the Engineering Experiment Station of the University of Illinois through its Department of Mining Engineering.) *Technical Paper* **284.** 32 pp. Paper, 10 cents.

Conditions in the Feldspar Industry. R. F. Ladoo. *Reports of Investigations* **2311.** 10 pp. Issued January 1922.

Growing Need for Preservation of Mine Timber. R. R. Hornor. *Report of Investigations* **2310.** 8 pp. Issued January 1922.

Low-Temperature Distillation of Amalgams of Bituminous Noncoking Coal and Asphaltic Oils. J. D. Davis and C. E. Coleman. *Reports of Investigations* **2312.** 7 pp. Issued January 1922.

Milling Methods in the Tri-State Zinc District. Progress of Investigation by U. S. Bureau of Mines, in coöperation with Missouri School of Mines and Metallurgy and Miamai (Okla.) School of Mines. W. H. Coghill and C. O. Anderson. *Reports of Investigations* **2314.** 14 pp. Issued January 1922.

Momentary Heating of Inflammable Coal Dusts. G. B. Taylor, H. C. Porter, and E. C. White. Foreword. G. S. Rice. *Reports of Investigations* **2306.** 20 pp. Issued January 1922.

Silica. R. B. Ladoo. *Reports of Investigations* **2307.** 7 pp. Issued January 1922.

Solubility of Oil Shales in Solvents for Petroleum. M. J. Gavin and J. T. Aydelotte. *Reports of Investigations* **2313.** Issued January 1922.

Bureau of Standards

An Investigation of Oxyacetylene Welding and Cutting Blowpipes with Special Reference to Their Economy in Operation, Safety, and Design. R. S. Johnston. *Technologic Paper* **200.** Paper, 35 cents.

Characteristic Soft X-Rays from Arcs in Gases and Vapors. F. L. Mohler and P. D. Foote. *Scientific Paper* **425.** Paper, 10 cents.

Recommended Specifications for Limestone, Quicklime, and Hydrated Lime for Use in the Manufacture of Glass. *Circular* **118.** Paper, 5 cents.

Thermal Expansion of Nickel, Monel Metal, Metal, Stellite, Stainless Steel, and Aluminium. W. H. Souder and Peter Hidnert. *Scientific Paper* **426.** Paper, 10 cents.

Congress

An Act to Grant Extension of Time under Gas and Oil Permits. Approved, January 11, 1922. Public No. 127, 67th Congress. H. R. 8344.

Metric System. Metric System, extracts from hearings before subcommittee on S. 2667, to fix metric system of weights and measures for certain uses, October 24, 1921. Statement by David A. Molitor. 11 pp.

Metric System. Metric System, hearings before subcommittee on S. 2267, to fix metric system of weights and measures as single standard of weights and measures for certain uses, October 24–28, 1921. Part II. 119 pp.

Hearings before the Committee on Finance, United States Senate, of the Proposed Tariff Act of 1921 (H. R. 7456). **Schedule I. Chemicals, Oils and Paints.** Revised and Indexed. 1344 pp. 1922.

Department of Commerce

Ninth Annual Report of the Secretary of Commerce, 1921. 149 pp.

Federal Trade Commission

Summary of Report of the Federal Trade Commission on the Pacific Coast Petroleum Industry. Part II. Prices and Competitive Conditions. 21 pp. Paper, 5 cents.

Geological Survey

Alaskan Mining Industry in 1921. A. H. Brooks. Bulletin 722-A. Separate from Mineral Resources of Alaska, 1920-A.

Artificial Gas and By-products in 1917-18. R. S. McBride. Separate from Mineral Resources of the United States, 1919, Part II. 62 pp. Published November 16, 1921.

Barytes and Barium Products in 1920. G. W. Stone. Separate from Mineral Resources of the United States, 1920, Part II. 11 pp. Published December 6, 1921.

Candelaria Silver District, Nevada. Adolph Knopf. Separate from Contributions to Economic Geology, 1922, Part I. 22 pp. Published January 20, 1922.

Cobalt, Molybdenum, Nickel, Tantalum, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1919. F. L. Hess. Separate from Mineral Resources of the United States, 1919, Part I. 19 pp. Published November 10, 1921.

Contributions to Economic Geology (Short Papers and Preliminary Reports), 1920. Part I—Metals and Nonmetals except Fuels. F. L. Ransome, H. S. Gale and E. F. Burchard. *Bulletin* **715.** 230 pp.

Contributions to Economic Geology (Short Papers and Preliminary Reports), 1920. Part II—Mineral Fuels. David White and M. R. Campbell. *Bulletin* **716.** 248 pp. 1921.

Forty-second Annual Report of the Director of the United States Geological Survey, Fiscal Year Ended June 30, 1921. 108 pp. December 1921.

Geologic Structure and Oil and Gas Prospects of a Part of Jefferson County, Oklahoma. H. M. Robinson. *Bulletin* **726–F.** Separate from Contributions to Economic Geology, 1921, Part II. 26 pp. Published December 20, 1921.

Gold and Silver in 1919. General Report. J. P. Dunlop. Separate from Mineral Resources of the United States, 1919, Part I. 45 pp.

Gold Lodes in the Upper Kuskokwim Region, Alaska. George C. Martin. *Bulletin* **722-E.** Separate from Mineral Resources of Alaska, 1920-E. 13 pp.

Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1920. Mines Report. C. G. Yale. Separate from Mineral Resources of the United States, 1920, Part I. 37 pp. Published November 25, 1921.

Gold, Silver, Copper, Lead, and Zinc in Idaho and Washington in 1920. Mines Report. C. N. Gerry. Separate from Mineral Resources of the United States, 1920, Part I. 40 pp. Published December 27, 1921.

Gold, Silver, Copper, Lead, and Zinc in Montana in 1920. Mines Report. C. N. Gerry. Separate from Mineral Resources of the United States. 1920, Part I. 25 pp. Published December 17, 1921.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1919. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1919, Part I. 15 pp. Published November 12, 1921.

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1920. Mines Report. V. C. Heikes. Separate from Mineral Resources of the United States, 1920, Part I. 29 pp. Published January 13, 1922.

Iron Ore, Pig Iron and Steel in 1920. E. F. Burchard and H. W. Davis. Separate from Mineral Resources of the United States, 1920, Part I. 35 pp. Published January 23, 1922.

Tin in 1919. Adolph Knopf and B. L. Johnson. Separate from Mineral Resources of the United States, 1919, Part II. Published January 26, 1922.

Water-Power Investigations in Southeastern Alaska. G. H. Canfield. *Bulletin* **722-B.** Separate from Mineral Resources of Alaska, 1920-B. 41 pp. 1921.

Zinc in 1920. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1920, Part I. 17 pp. Published December 19, 1921.

Public Health Service

Carbon Monoxide Poisoning in Closed Garages. Reprint **694** from Public Health Reports. 6 pp. Paper, 5 cents.

Lead Poisoning in Pottery Trades. B. J. Newman, W. J. McConnell, O. M. Spencer, and F. M. Phillips. *Bulletin* **116.** 22 pp. Paper, 35 cents.

MARKET REPORT—FEBRUARY, 1922

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Feb. 1	Feb. 15
Acid, Boric, cryst., bbls	lb.	.12¾	.12¾
Hydrochloric, com'l, 20°	lb.	.01¼	.01¼
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.06¾	.06¾
Phosphoric, 50% tech	lb.	.12	.10
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66° tks. wks.	ton	16.00	16.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb.	.03½	.03½
Aluminium Sulfate (iron-free)	lb.	03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	.07½	.07½
Ammonia Water, drums, 26°	lb.	.07½	.07½
Arsenic, white	lb.	.07¼	.07½
Barium Chloride	ton	50.00	55.00
Nitrate	lb.	*.06½	*.06½
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works,	100 lbs.	2.00	2.00
Borax, cryst., bbls	lb.	.05¾	.05¾
Bromine, pure	lb.	.20	.20
Calcium Chloride, fused, f. o. b. N. Y.	ton	24.75	24.75
Chalk, precipitated, light	lb.	.04	.04
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.55	5.55
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.80	4.05
Lead Acetate, white crystals	lb.	.11	.11
Nitrate	lb.	.15	.15
Red American	100 lbs.	.08	.08
White American	100 lbs.	.07¼	.07¼
Lime Acetate	100 lbs.	1.75	1.75
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, tech	lb.	.06	.06
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*48.00	*49.00
Phosphorus, yellow	lb.	*.25	*.25
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.10	.10
Bromide, imported	lb.	*.14	*.14
Carbonate, calc., 80–85%	lb.	.04½	.04½
Chlorate, cryst	lb.	*.05½	*.05½
Hydroxide, 88–92%	lb.	*.05¾	*.05¾
Iodide, bulk	lb.	2.90	3.15
Nitrate	lb.	.08	.08
Permanganate, U. S. P.	lb.	*.14	*.14
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.44½	.44½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	*1.75	*1.65
Caustic, 76%	100 lbs.	*3.50	*3.30
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.30	2.30
Bichromate	lb.	.07¾	.07¾
Chlorate	lb.	.07	.07
Cyanide	lb.	.26	.26
Fluoride, technical	lb.	.09	.09
Hyposulfite, bbls	100 lbs.	3.50	3.25
Nitrate, 95%	100 lbs.	2.37½	2.35
Silicate, 40°	lb.	.01	.01
Sulfide, 60% fused	lb.	*.04¼	*.04¼
Bisulfite, powdered	lb.	.04½	.04½
Strontium Nitrate	lb.	*.10	*.10
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride. .50% sol'n	lb.	.10¼	.10¼
Oxide	lb.	.38	.38
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.08	.08

ORGANIC CHEMICALS

		Feb. 1	Feb. 15
Acetanilide	lb.	*.29	*.32
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.09	.09
Acetylsalicylic	lb.	.80	.80
Benzoic, U. S. P., ex-toluene	lb.	.60	.60
Carbolic, cryst., U. S. P., drs.	lb.	.11	.12
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	*.43	*.44
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.14	.14
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.24	.24
Tartaric, crystals, U. S. P.	lb.	*.25	*.24
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12½	.12½
Alcohol, denatured, complete	gal.	.40	.35
Ethyl, 190 proof	gal.	4.85	4.85
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap, refined	lb.	.96	.93
Carbon Bisulfide	lb.	.06½	.06
Tetrachloride	lb.	.10½	.10½
Chloroform, U. S. P.	lb.	*.37	*.37
Creosote, U. S. P.	lb.	.40	.40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.79	2.89
Imported Potato	lb.	.08½	.08½
Ether, U. S. P., conc., 100 lbs.	lb.	.14	.14
Formaldehyde	lb.	*.10	*.09½
Glycerol, dynamite, drums	lb.	.15	.15
Methanol, pure, bbls	gal.	.75	.75
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	2.22	2.32
Potato, Jap	lb.	.06	.06
Rice	lb.	.18	.18
Sago	lb.	.04	04

OILS, WAXES, ETC.

		Feb. 1	Feb. 15
Beeswax, pure, white	lb.	.33	.33
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10½	.10½
Ceresin, yellow	lb.	.07½	.08
Corn Oil, crude, tanks, mills	lb.	.06¾	06¾
Cottonseed Oil, crude, f. o. b. mill	lb.	.07⅜	.08
Linseed Oil, raw (car lots)	gal.	.77	.86
Menhaden Oil, crude (southern)	gal.	.38	.42
Neat's-foot Oil, 20°	gal.	1.32	1.32
Paraffin, 128–130 m. p., ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.35	5.45
Rosin Oil, first run	gal.	.36	.36
Shellac, T. N.	lb.	.66	.67
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.77	.77
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.93	.91

METALS

		Feb. 1	Feb. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.45	4.45
Bismuth	lb.	1.55	1.65
Copper, electrolytic	lb.	.13⅜	.13½
Lake	lb.	.13½	.13½
Lead, N. Y.	lb.	.04¾	.04¾
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	93.00	93.00
Quicksilver, flask	75 lbs. ea.	48.00	49.00
Silver, foreign	oz.	.66¼	.66¼
Tin	lb.	.31¼	.31½
Tungsten Wolframite	per unit	2.50	2 50
Zinc, N. Y.	100 lbs.	4.85	4.80

FERTILIZER MATERIALS

		Feb. 1	Feb. 15
Ammonium Sulfate, export	100 lbs.	2.60	2.60
Blood, dried, f. o. b. N. Y.	unit	3.50	3.50
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works	unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.75	.75
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.00 & .10	3 00 & .10

*Resale or Imported (not an American maker's price).

COAL-TAR CHEMICALS

Crudes

		Feb. 1	Feb. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.29	.29
Cresol, U. S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	.07½	.07½
Phenol, drums	lb.	.11	.12
Toluene, pure	gal.	.30	.30
Xylene, 2 deg. dist. range	gal.	.45	.45

Intermediates

		Feb. 1	Feb. 15
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.00	2.00
H	lb.	.90	.90
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.30	2.30
Naphthionic, crude	lb.	.65	.65
Nevile & Winther's	lb.	1.30	1.30
Phthalic	lb.	.32	.32
Picric	lb.	.20	.20
Sulfanilic	lb.	.27	.24
Tobias'	lb.	1.60	1.60
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.17	.17
Aniline Salt	lb.	.22	.20
Anthraquinone	lb.	1.50	1.40
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.25	1.25
Benzidine (base)	lb.	.90	.90
Benzidine Sulfate	lb.	.70	.70
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	.60	.60
Dimethylaniline	lb.	.38	.38
Dinitrobenzene	lb.	.21	.21
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.60	.60
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.35	1 35
Metol (Rhodol)	lb.	3.50	3.50
Monochlorobenzene	lb.	.10	.10
Monoethylaniline	lb.	1.00	1.00
a-Naphthylamine	lb.	.30	.30
b-Naphthylamine (Sublimed)	lb.	1.50	1.50
b-Naphthol, dist	lb.	.30	.30
m-Nitroaniline	lb.	.85	.85
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	.11½	.11½
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	—	—
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.70	.70
m-Phenylenediamine	lb.	1.10	1.10
p-Phenylenediamine	lb.	1.60	1.60
Phthalic Anhydride	lb.	.35	.35
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	2.00	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.40	.40
Tolidine (Base)	lb.	1.20	1.20
Toluidine, mixed	lb.	.30	.30
o-Toluidine	lb.	.20	.20
p-Toluidine	lb.	1.00	1.00
m-Toluylenediamine	lb.	1.10	1.10
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Feb. 1	Feb. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50

Acid Colors (*Concluded*)

		Feb. 1	Feb. 15
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Alkali Blue, domestic	lb.	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Feb. 1	Feb. 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	1.10	1.10
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Feb. 1	Feb. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Feb. 1	Feb. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.75	.75

Chrome Colors

		Feb. 1	Feb. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.55	.55
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Feb. 1	Feb. 15
Auramine, O, domestic	lb.	1.80	1.80
Auramine, OO	lb.	2.50	2.50
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	2.25	2.25
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	1.60	1.60
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc	lb.	8.50	8.50
Victoria Blue, base, domestic	lb.	3.50	3.50
Victoria Green	lb.	1.50	1.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of
INDUSTRIAL & ENGINEERING CHEMISTRY
Published Monthly by The American Chemical Society

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(One Madison Ave., New York City)

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Advertising Department:
170 Metropolitan Tower
New York City
Telephone: Gramercy 2145

Volume 14 APRIL 1, 1922 No. 4

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Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, $1.00, Canada, Cuba and Mexico excepted.
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Member of Audit Bureau of Circulations

EDITORIALS

The President's Message

Following the daily duties of the laboratory; reading journals devoted to pure and applied chemistry; listening to discussions by chemists of things near to chemists, thoughts come, on which I ponder earnestly. These thoughts shape themselves into questions addressed to myself. They are so addressed that I may learn, if possible, how I really stand on the subjects constantly coming to mind. Usually, I start with the premise that I am an American—my whole family history crying out to me that I am an American. Naturally, it follows that my first duty then is to stand for my country in everything vitally affecting her. That, she expects of me. If she enters upon projects looking to her own advancement among sister nations, it is surely incumbent upon me to lend a helping hand, remembering that the greatest battles in the life and development of a nation are fought not in time of war, but in times of peace.

The consciousness that my country is endeavoring to establish throughout its length and breadth industries, having underlying chemical bases, makes it my bounden duty as an American chemist to sacrifice apparent personal interests that her ambitions and desires may be realized.

I know that ever since the United States came into existence the Republic has sought to develop along industrial chemical lines. I recall an enthusiastic, loyal group of American pioneers in chemistry, laboring without hope of fee or reward, for their country—to create an independent chemical industry in their homeland. Shall this spirit be permitted to die?

To-day, I behold my country far advanced in chemistry; eager to make herself quite independent; and yet the goal, to which she looks and toward which she is struggling, is threatened. Our industries, splendid as they have become, are menaced. There are so many conflicting interests pushing to the front. We say we desire absolute commercial and intellectual independence, and yet do not our acts belie our words? Which shall it be, I query of myself? Is it country or is it self which is to prevail in the great domain of chemistry?

Thus ruminating, it is recalled when the early states had won their independence and sat down to agree upon a broad constitution of rights, dissensions arose; and that for which blood had been shed and upon which every hope for future welfare rested was in danger of being lost forever. That early scientist, Franklin, said when driven to despair by the fear of losing all, "We shall be divided by our little, partial, local interests; our projects will be confounded, and we, ourselves, shall become a reproach and a by-word down to future ages."

With these words ringing in my ears, I determine "that as for me and my house" we shall stand for everything making for an independent chemical industry, for those who manufacture or may manufacture products required in the pursuit of the science on a large scale or on a scale convenient for educational research and teaching, and for those things which will insure our country's absolute independence in the many ramifications of the greatest of all sciences—chemistry.

EDGAR F. SMITH

The Engineers Line Up

The American Engineering Council, the governing body of the Federated American Engineering Societies, passed the following report of its Public Affairs Committee at the last Council meeting.

WHEREAS, what is known as the Chemical Dye Embargo, provided in Title V of the Emergency Tariff Act, which will expire with the enactment of the permanent tariff bill, and

WHEREAS, this Title was excluded from the regular tariff bill now before the House of Representatives, and

WHEREAS, the development of the chemical industry of the United States is especially important in times of war,

Be it resolved, that American Engineering Council approves in principle Title V of the Emergency Tariff Act and urges that either this Title or other similar provisions be included in the regular tariff bill.

The Council speaks for approximately 50,000 engineers who thus register their support of the coal-tar chemical industry.

Actomism

A little while ago, in response to an expressed need for some word which would indicate optimism plus action, the word "actomist" was coined. An actomist is an optimist who makes the most of every opportunity to apply his optimism and who does not confine his efforts to breezy sayings. This is an opportune time to interest chemists in actomism. The industries are going through very trying times, partly caused by an increase in capacity for production so large that the former normal market is insufficient. Our exports for the eight months ending February 1922 were about 46 per cent greater in value than in 1913. For the eight months ending February 1922 our exports were valued at $2,480,425,797 and imports at $1,622,866,436. Chemists after all have greater justification for optimism than most. A country producing so large a percentage of the necessities of life as come from the United States cannot remain long in an unfavorable position. Of the world's wheat we produce 22 per cent, oats 35 per cent, cotton 60 per cent, corn 80 per cent, dairy products 25 per cent, pig iron 50 per cent, petroleum 50 per cent, paper 45 per cent, glass 25 per cent, steel products 50 per cent. These typical industries and many others depend in some way or other upon chemistry for their advancement and their prosperity. We have already seen signs of increased interest on the part of manufacturers in what chemistry and chemists can do for them. We know that many industries must have large export markets if their production is to reach an economical stage. We know, too, that in foreign markets protection cannot be expected. There is only one answer. Research must be consistently and continuously supported if industry as a whole is to maintain its position. But before industry can engage in research upon an adequate scale it must have encouragement at home.

The Bureau of Foreign and Domestic Commerce will establish a Chemical Division about July 1. This Division will maintain an intimate contact with manufacturers and will guide the activities of the thousand government representatives abroad, thus rendering improved service to our chemical manufacturers.

A Blessing in Disguise

The investigation by the Senate Committee, to determine whether there is a monopoly of the dyestuffs industry in America and to what extent efforts have been made to influence legislation, got under way after several ineffectual efforts.

Those who heard the statement of the prosecution, represented by Senator King of Utah, were struck by the large number of inexcusable errors in the statements and were impressed with the fact that the Senator really knew very little of what is supposed to be common knowledge. His statement has proved to be a blessing in disguise, for the way has been opened for the presentation of many facts and a quantity of data which could not otherwise have been offered in full. Not only have the errors contained been disproved, but many have been shown to be entirely without foundation, resting on rumors and alleged facts. The opposition has not even taken the trouble to cross-examine many of the witnesses who have been heard thus far, and it is significant that all of those who have appeared have come without subpoena and have shown every effort to assist the Committee.

An amusing example of error is to be found in the stress laid upon two items of the financial statement of the American Dyes Institute, one a rent item of $40 and the other a $3000 dinner given in Washington to the National Cotton Manufacturers Association by the Institute. The real facts are that the $3000 item was for rent paid for offices in New York, while the $40 item covered the traveling expenses of the Secretary of the Institute who attended the regular dinner of the Cotton Manufacturers, which was held not in Washington but in Boston.

One after another, those who have testified have declared in response to direct questions that in their opinion no monopoly exists and that no monopoly can exist in an industry composed of so many parts. It has been pointed out that no one concern can ever hope to make more than a small percentage of the compounds needed. Man after man, whether from the industry or with other connections, has stated his belief that the limited or selective embargo, with a tariff to assist in stopping embargo leaks, is the only satisfactory way to encourage the chemical industry during the next ten years. After that it will be in a position to meet all competition without special assistance, and will stand a fair chance of taking the place in the world, chemically speaking, formerly occupied by Germany.

As we go to press witnesses continue to present themselves, make their statements under oath, and endeavor to describe fully and in detail the exact situation with respect to the chemical industry and the efforts which have rightfully been made to present a true picture of that industry in its many relations to the American public.

We are interested in what is to come from the investigation. Will it be possible to bring into the open the anti-American interests which are steadily at work, and the real influences behind the scenes which have led to the present situation? We are not interested in reading further volumes of Senate hearings. It would be unjust to consume the time of so many executives and technical men to no purpose. From this hearing we hope there will come a clear understanding of industrial chemistry in all its relationships. We would have Congress understand its meaning to our educational program, our scientific research in many fields, and our desire firmly to establish the American industry. The probe will fall short of what is needed if it fails to clear the situation and make it possible to form a definite policy for immediate application.

Efficiency in the Chemical Warfare Service

The treaty to abolish poison gases does not in any way abolish chemical warfare. In fact, it is carefully brought out in the treaty that the nations do not contemplate giving up research incident to preparedness. The Chemical Warfare Service is just as essential to the Army and Navy today as it ever was. The treaty does not prohibit nontoxic gases, protective smokes, and the like. It does not concern research, development, and proving, which must be continued.

The Chemical Warfare Service requested an appropriation of $4,500,000. This was later reduced by them to $1,500,000, as the minimum scale for research, the maintenance of the arsenal at Edgewood, and the purchase of necessary supplies. The present item in the appropriation bill is $500,000, the reduction being made in the War Department before the bill was sent to Congress. If this amount is not increased it will be impossible to maintain in a stand-by condition the plant at Edgewood, costing millions of dollars, supplies must be limited, and the organization must be reduced to not more than three hundred men, who can accomplish comparatively little upon the great number of pressing problems which should be attacked.

The American Chemical Society feels a peculiar pride in the Chemical Warfare Service. It was active in its establishment. It has a responsibility for its future.

The Earning Power of Research

From among the many samples of research which has paid not only in money but in direct benefits to mankind we may cite research supported by the American Telephone and Telegraph Company, and particularly by its subsidiary, the Western Electric Company. Beginning with studies on the radioactivity of matter, the audion bulb has been developed. To this device we owe much. The ability to admit, by means of the audion, energy from storage batteries to strengthen sound waves without altering their other characteristics makes possible the present satisfactory long distance telephone message. Losses on the lines can be replaced, and a proper balance can be obtained under difficult conditions. It is also vital to wireless telephony and has applications in the field of scientific research which are just being investigated. Its use in ear phones which permit anyone who can use a telephone to hear conversations without the annoyance which is so frequently experienced with other devices bids fair to be a blessing. Its earning power can best be realized when it is recalled that other lines of research upon the problem of increasing the useful radius of telephonic communication involved the reconstruction of all telephone instruments. This research made it possible to extend the useful radius of every existing telephone more than a thousand miles without the large expenditure otherwise necessary. From the experiences of the industrial group in question a long list of examples might be taken to show the earning power of research. For it is only through the continual quest of new scientific facts and their application to the problems of communication that it has been possible to serve the public efficiently and at reasonable cost.

The first reply to our request in the February JOURNAL for data descriptive of the "Earning Power of Research" is the article on Pyrex, printed on page 336 of this issue. We hope that this acceptance of our invitation will be followed by many others.

The U. S. Government Explosives Plant, Nitro, West Virginia[1]

I—Some Phases of the Organization, Design, Construction, and Operation

By **March F. Chase**[2]

L. L. Summers & Co., 140 Nassau St., New York, N. Y.

After the entry of the United States into the war, it became evident that the requirements for propellent powder would greatly exceed the production from government and private plants.

While large private plants had been built in this country after the start of the European war, the undertaking of building a government plant involving such a highly technical subject as smokeless powder required a very careful and intensive study of methods of design and construction.

In the beginning there were five essential requirements:

1—That the plant should be an integrated one and be built directly by the War Department.
2—That it should produce the quantity and quality of powder specified.
3—That the construction proceed as rapidly as possible.
4—That construction materials be conserved to the greatest extent possible.
5—That it be designed to operate as efficiently as possible as regards the consumption of raw materials.

It is the object of this paper to show the general methods used to accomplish the above and to give for illustrative purposes a detailed description of how the policies adopted worked out in the design of special units.

In the beginning one must get clearly in mind that the problem handed to the director was simply to build on a selected site a smokeless powder plant to produce 625,000 pounds of smokeless powder per day and to have this production available within the shortest possible time.

An integrated smokeless powder plant involves six highly technical operations in addition to the general operations incident to every industrial plant:

1—Manufacture of sulfuric acid.
2—Manufacture of nitric acid.
3—Cotton purification and bleaching.
4—Nitrating of cotton.
5—Colloiding of nitrocellulose.
6—Drying of smokeless powder.

As a first step there was established a separate unit of the War Department designated United States Explosives Plants. Mr. D. C. Jackling was appointed director and was given extremely broad powers. With nothing but a commission and a plant site, Mr. Jackling started in December 1917 to build the largest completely integrated smokeless powder plant ever attempted in this country. The first manufacturing unit was started in June 1918 and the first powder was produced September 14, 1918.

As the first step in developing his organization the director established three divisions:

1—Director's staff.
2—Contractor's organization in charge of field work.
3—Architectural organization.

The director's staff was recruited from civil life and included experts in every line of activity involved in the operation. This staff supplied the information for the architects, approved plans and specifications, approved purchase contracts for the construction department, made payments to vendors on vouchers from the construction department, and took charge of relations between the U. S. Explosives Plants unit and other governmental bureaus. A skeleton organization was soon formed, by appointment, of a number of men to the director's staff, of a large contracting firm to take charge of field work, and a firm of architects to direct the preparation of the plans.

The personnel of these three divisions was rapidly augmented by the services of men and organizations to take over certain special lines of work, but throughout the entire construction work no modification was made in this plan of the three separate general divisions.

It was quite obvious that at the outset old established methods of procedure could not be followed as the time was limited and the construction work, design, statement of requirements, and equipment ordering all had to proceed at the same time. The work was still further complicated by the fact that continual changes had to be made in design on account of rapidly changing methods of manufacture and the necessity of substitution of equipment because of the lack of time to obtain certain standard equipment.

Starting with the basic requirements—cotton, alcohol, sulfuric and nitric acid—there had to be developed the total requirements for the complete plant. This was done as follows:

A simple flow sheet was first prepared showing the amount of basic raw materials. This was then submitted to expert engineers, each one preparing a rough flow sheet as to the requirements in his particular subject. These figures were then put together to establish a general idea of the magnitude of each operation. At the same time the architects started the design of plant units; as an example, the design of one sulfuric acid unit was started, the design of one cotton purification building was started, the design of one powder mixing house was started. At the same time a general plant layout was prepared and arbitrarily a site was selected for the first housing. This permitted the field workers to start work on temporary housing for construction workers.

The next step was to create a small board or committee within the director's staff, of men who were generally familiar with all operations connected with smokeless powder manufacture. Then each operation was assigned to a separate engineer who was a specialist in his particular subject. Architects divided their work in a similar manner and each expert of the director's staff worked directly with the group of draftsmen preparing the plans on the unit in which the expert was interested.

A brief general description of the process and plant follows in order to give a clear understanding of just how the system of design and construction was applied.

Smokeless powder, or colloided nitrocellulose, the most extensively used propellant in the World War, is manufactured in the United States by nitrating with mixed acid (21.5 per cent of 100 per cent nitric acid, 63 per cent of 100

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[1] Received February 27, 1922.

[2] Consulting Engineer. Formerly Assistant Director of U. S. Government Explosives Plants; formerly member of War Industries Board.

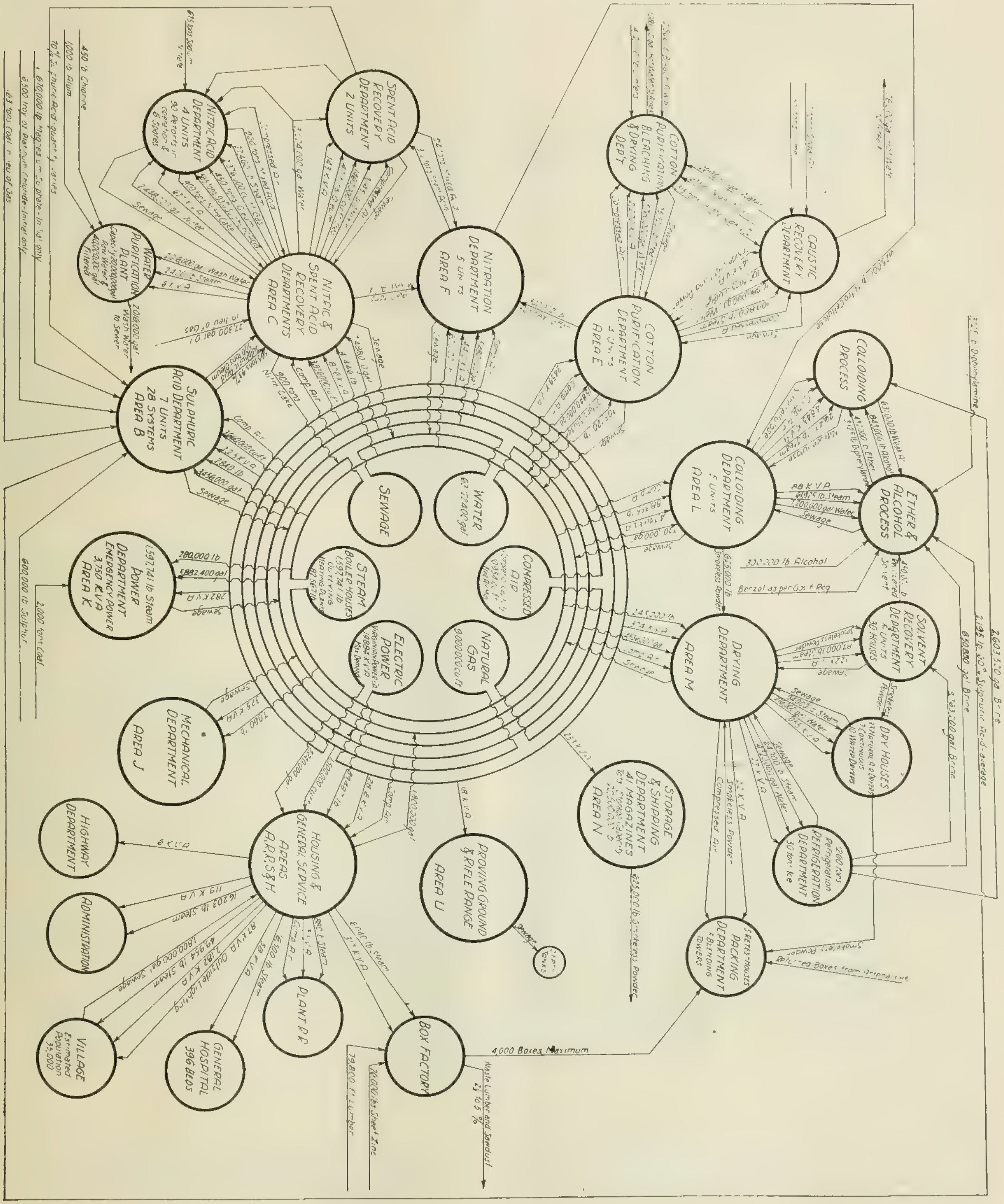

NITRIC ACID DEPARTMENT 4 UNITS
SPENT ACID RECOVERY DEPARTMENT 2 UNITS
WATER PURIFICATION PLANT
NITRIC & SPENT ACID RECOVERY DEPARTMENTS AREA C
NITRATION DEPARTMENT 5 UNITS AREA F
COTTON PURIFICATION BLEACHING & DRYING DEP'T
CAUSTIC RECOVERY DEPARTMENT
COTTON PURIFICATION DEPARTMENT 4 UNITS AREA E
COLLOIDING PROCESS
SULPHURIC ACID DEPARTMENT 7 UNITS 28 SYSTEMS AREA B
COLLOIDING DEPARTMENT 5 UNITS AREA L
ETHER & ALCOHOL PROCESS
SEWAGE
WATER
STEAM
COMPRESSED AIR
ELECTRIC POWER
NATURAL GAS
POWER DEPARTMENT EMERGENCY POWER 3,750 KVA AREA K
DRYING DEPARTMENT AREA M
SOLVENT RECOVERY
DRY HOUSES
MECHANICAL DEPARTMENT AREA J
STORAGE & SHIPPING DEPARTMENT 41 MAGAZINES AREA N
REFRIGERATION DEPARTMENT
HIGHWAY DEPARTMENT
HOUSING & GENERAL SERVICE AREAS A,R,S&H
PROVING GROUND & RIFLE RANGE AREA U
ADMINISTRATION
PACKING DEPARTMENT
PLANT R.R.
BOX FACTORY
VILLAGE Estimated Population 35,000
GENERAL HOSPITAL 396 BEDS
4,000 Boxes Maximum
450 lb Chlorine
1000 lb Alum
600,000 lb Sulphur
2,000 tons Coal
300,000 lb Alcohol
Benzol as per G.O.T. Req.
280,000 lb
5,882,400 gal
282 KVA
Sewage
Comp. Air
88 KVA
1,200,000 gal Water
6 KVA
119 KVA

Fig. 1

General Notes

Sulfuric Acid Plant—Contact Process

Nitric Acid Plant Sodium Nitrate Distillation Process

Spent Acid Recovery Plant—Steam Denitration Process, Duriron Cascade System, Concentration Process

Mechanical Department—General Maintenance Shops, Operating Tools and Supplies

Power Plant—

Boiler Houses: 34—1043 rated horse power Boilers

Power House: 3—1250 KVA Turbo-generators
6—1145 cu. ft. per min. Air Compressors
8—6000 gal. per min. Filtered-Water Pumps

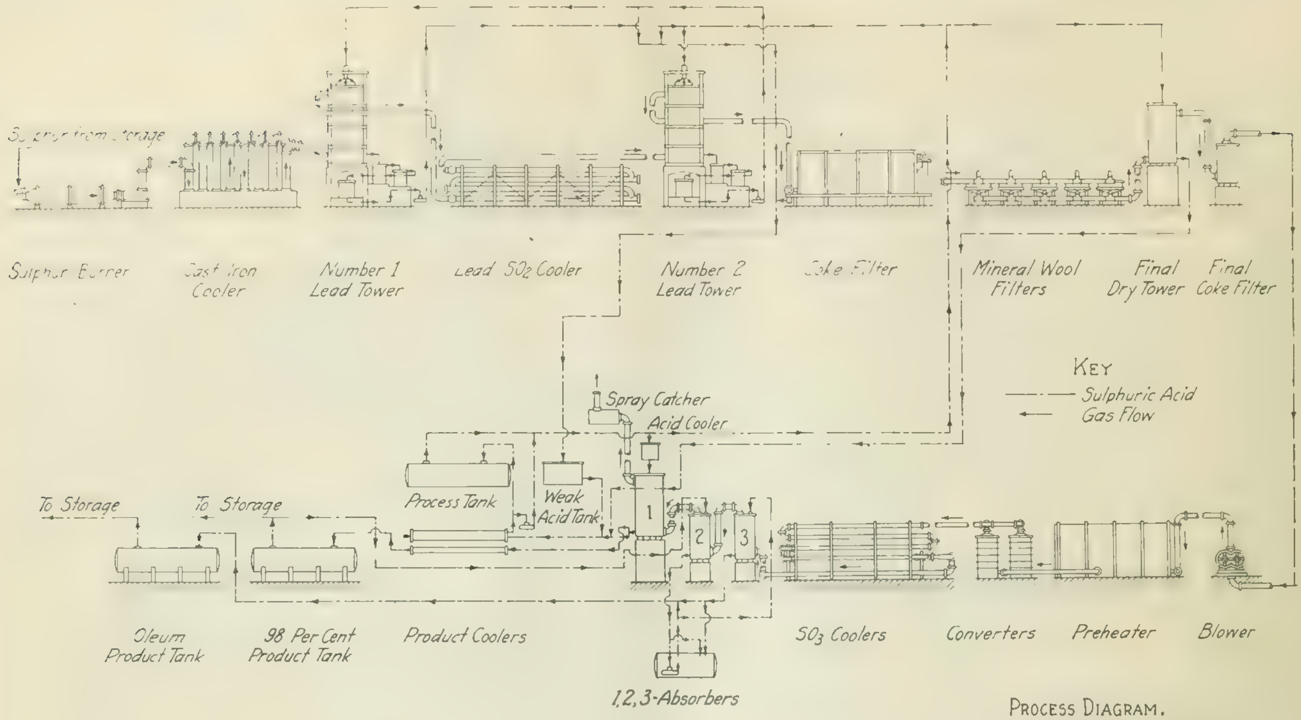
Power House: 3—2500 gal. per min. Fire Pumps
2—2500 gal. per min. Booster Pumps

Refrigeration Plant—Absorption System

Note—Capacities and requirements given are for a 24 hour period except for Steam and Electric Power. The quantities of Steam are given in pounds per hour. The figures given for Electric Power are the probable maximum rates of demand.

Figures given do not include the requirements of proposed extensions to the Village.

Quantities for Compressed Air and Sewage are not given on account of totals not being available.



PROCESS DIAGRAM.
U S GOVERNMENT EXPLOSIVES PLANT "C."
NITRO, W. VA.
SHEET 1 OF 10.
AREA B

per cent sulfuric acid, and 15.5 per cent water) a thoroughly digested mixture of varying proportions of cotton linters and hull fiber after they have been purified and bleached. The spent acids are removed by centrifuging and the nitrocellulose is then purified by boiling and pulping in a manner similar to the purification of wood pulp. The resulting nitrocellulose has an N_2 content of 12.50 to 12.70 per cent. To make the smokeless powder, the nitrocellulose is colloided with ether containing diphenylamine, a stabilizer, after the last trace of water has been displaced by ethyl alcohol under hydraulic pressure. The alcohol, with the ether, also acts as a solvent in forming the colloid. The chemically finished powder is then run through a finishing press known as a "macaroni press" which squeezes it through dies of the required cross section. The strings of powder are then granulated, *i. e.*, cut to proper length. After the excess solvent has been recovered and the powder thoroughly dried, it is blended with other lots to give uniformity. It is then ready for packing and shipment. These various processes require a period of approximately 30 days.

RAW MATERIALS

The raw materials necessary for the manufacture of smokeless powder are cotton, caustic, bleach, nitric acid, sulfuric acid, alcohol, ether, diphenylamine, and water. Large quantities of steam, electricity, and compressed air are also consumed.

To produce 625,000 lbs. of smokeless per 24-hr. day during the war, when the industries producing the raw materials were already overtaxed, it was necessary also to manufacture the nitric and sulfuric acid and the ether. Furthermore to produce this quantity of powder economically called for the recovery and restoration of the "black" caustic from the cotton purification, the spent acid from the nitrating, and the residual solvent alcohol and ether from the colloiding parts of the process.

The quantities of water, steam, gas, electricity, and compressed air used in the process and the waste sewage resulting therefrom necessitated the installation of all these utilities. As it would be manifestly impossible to erect an explosive plant in the vicinity of a city capable of housing the employees, it was decided that a complete town would have to be erected. It was decided by the Government that the plant should be located on the east bank of the Great Kanawha River about sixteen miles west of Charleston, W. Va. A tract of ground of sufficient size, shape, and topography suitable for the construction of a plant of this type, with fairly good facilities for the transportation of the raw materials and supplies by rail and by water, with large developed supplies of coal, oil, and natural gas nearby, and with a city of considerable number of employees during the early period of the construction of the plant, and with a strategic location with reference to the points to which the finished product was to be shipped, were the reasons for selecting this site.

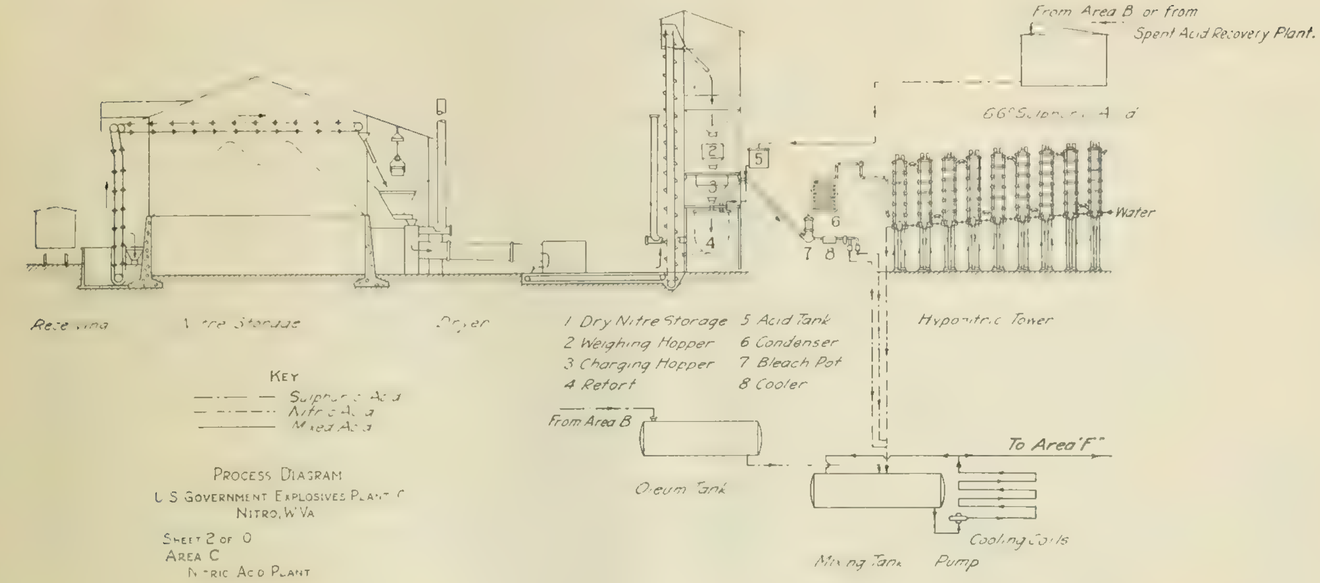
The name "Nitro" given to the plant and town is an abbreviation of the word "nitrocellulose."

PLANT SUBDIVISIONS

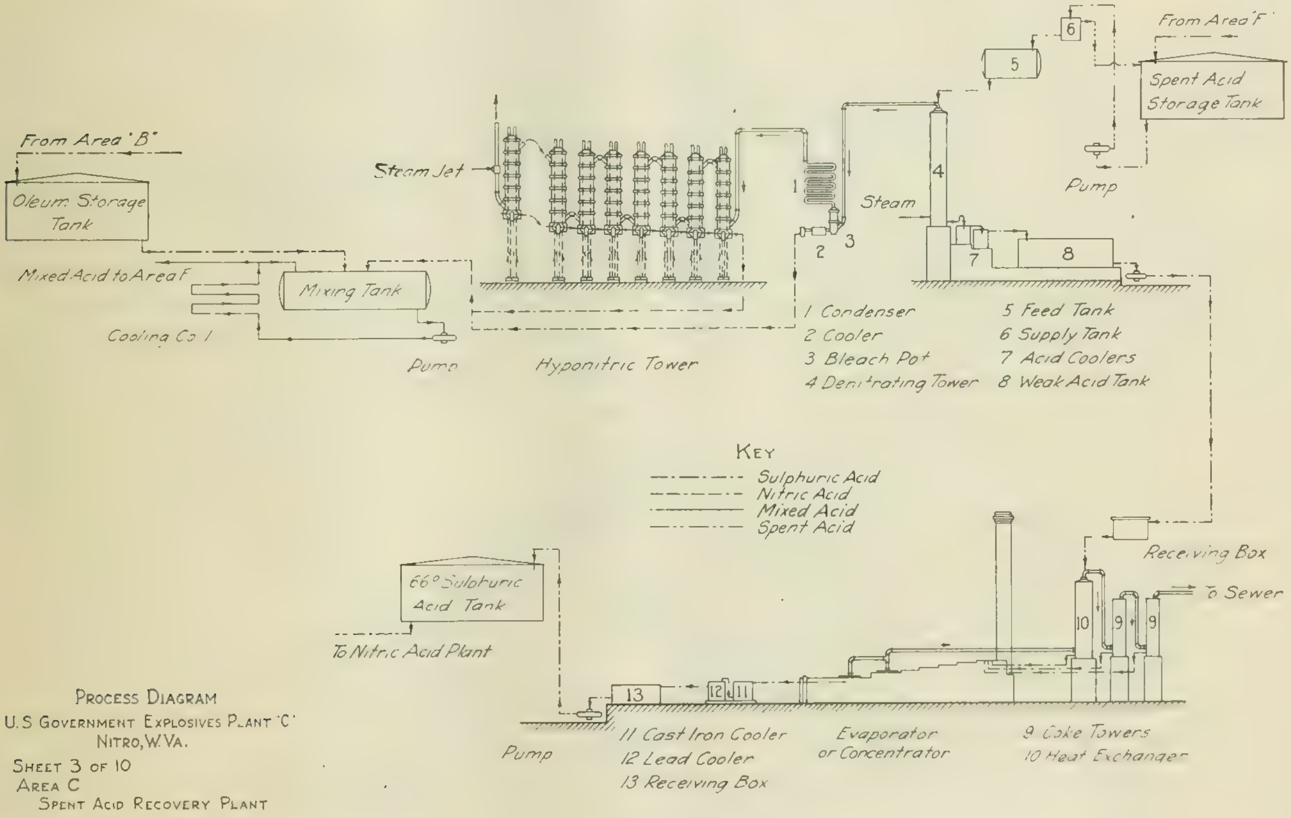
The plant was divided into the following areas:

I—PLANT AREAS:

- B—Sulfuric acid
- C—Nitric and spent acid recovery
- E—Cotton purification and bleaching
- F—Nitration pulping and purification
- H—Administrative box factory highway and plant railroad
- J—Mechanical
- K—Power department and power distribution
- L—Colloiding
- M—Drying
- N—Storage and shipping
- U—Proving ground and rifle range



PROCESS DIAGRAM
U. S. GOVERNMENT EXPLOSIVES PLANT "C"
NITRO, W. VA.
SHEET 2 OF 10
AREA C
NITRIC ACID PLANT



PROCESS DIAGRAM
U. S. GOVERNMENT EXPLOSIVES PLANT "C"
NITRO, W. VA.
SHEET 3 OF 10
AREA C
SPENT ACID RECOVERY PLANT

2—HOUSING AREAS:

A—Foreign and colored employees' quarters
O—Skilled mechanics' quarters and recreation grounds
P—Skilled mechanics and unskilled white Americans
R—Executive residences, skilled mechanics and civic center
S—Skilled mechanics and military guards and general hospital

To conform to the general scheme of dividing the plant into geographic areas, certain technical areas were created which were common to one or more areas:

3—TECHNICAL AREAS:

D—Plant railroads and equipment
G—Buildings and structures
Q—Fire protection and safety
T—Water works and distributions
V—Sewerage
W—General equipment and construction
X—Preparation of site
Y—Chemical laboratories
Z—Municipal organization and welfare
ZZ—Gas distribution

The power plant, administration, and mechanical areas were centrally located, and the processes were grouped around these in such a way that the product would flow naturally from one to the other.

UNIT SYSTEM OF PRELIMINARY DETERMINATION

In the design there were two kinds of requirements that had to be always kept in mind: those that would be pro-

TABLE I Unit System of Preliminary Determination Based on Production of 625,000 Lbs. of Smokeless Powder per 24-Hr. Day

ITEM	TOTAL AMOUNT	UNIT	UNIT AMOUNT PER LB. FINISHED SMOKELESS POWDER
		Raw Materials	
Sulfur	600,000	Lbs. per 24 hrs.	0.96
Sodium nitrate	1,350,000		2.16
Raw cotton	550,000		0.88
Soda ash	34,000		0.0544
Lime	110,000		0.176
Bleach	12,500		0.020
Diphenylamine	3,125		0.005
Ethyl alcohol	300,000		0.480
Sheet zinc	26,000		0.0416
Lumber	79,800	Bd. ft. per 24 hrs.	0.1278
		Utilities	
Water:			
Raw	30,174,000	Gals. per 24 hrs.	48.24
Filtered	32,112,000	Gals. per 24 hrs.	51.37
Total	62,286,000	Gals. per 24 hrs.	99.61
Gas	8,996,000	Cu. ft. per 24 hrs.	14.38
Coal	2,000	Tons per 24 hrs.	0.0032
Steam	1,680,308	Lb. per hr.	2.6881
Electricity	19,884	KVA max.	0.0319
Refrigeration:			
Brine cooling equiv. melting ice	1,260	Tons per 24 hrs.	0.002
Ice making	50	Tons per 24 hrs.	0.00008
Compressed air	10,954	Cu. ft. free air per min.	0.0175
Sewers:			
Sanitary	250	Gals. per cap. per 24 hr.	
Storm	1	Inch rainfall per hr.	

vided from outside sources, and those that would be taken care of by other departments of the plant.

The flow sheets, both general and detailed, did not differentiate between these two kinds of requirements. They were ordinary flow sheets as commonly prepared in any engineering undertaking, the only new features possibly being the form of the final flow sheet which is shown in Fig. 1, p. 261.

To preserve at all times in the design a perfectly balanced plant, it was necessary to devise an accurate and flexible system of stating full requirements that were to be provided for any department from general plant operations. This was accomplished by gathering on charts the requirements which a department had to provide for other departments and reducing the totals to units per pound of smokeless powder. For want of a better term, this system was designated the unit system of preliminary determination. In all there were about twenty of these charts prepared, and none of them were finished until the design and construction had been practically completed. From these charts the total raw material requirements were tabulated and are shown in final form in Table I. Tables II and III are copies of the final chart prepared for the utilities. These charts were being continually corrected and revised as time went on. Any change in process or in design was immediately noted on these charts, and each one that was affected by the change was corrected so that the board of governing engineers had at any time a complete statement of the total capacities of every kind to be arranged for.

In addition to the flow sheets and unit charts there were prepared diagrammatic process charts which are illustrated in Sheets 1 to 9, inclusive. These process charts were to enable draftsmen and engineers unacquainted with the process to get at a glance the general design and flow of material in a given process.

The whole system of organization for the design was thus carried out with little or no confusion and a minimum chance of error, and a very short time was required for establishing a complete file of data. It was found that the designing work could proceed in all departments at the same time and if it was necessary to change the design in any department its effect on any other department was immediately taken care of with practically no loss of time. The engineers in charge of the preparation of the requirement charts were all experts in their particular line and they were afterwards used as supervising engineers in the construction department.

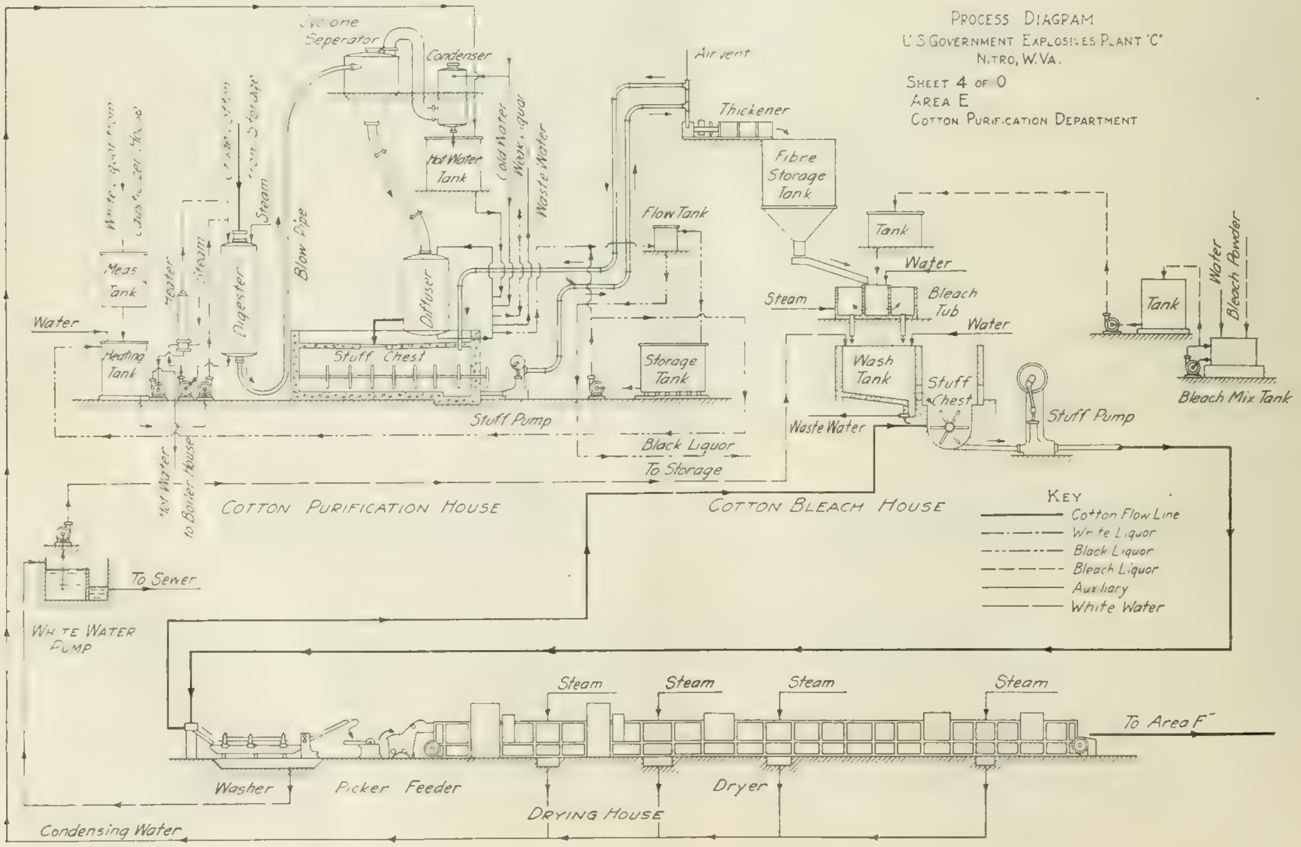


TABLE II—UNIT SYSTEM OF PRELIMINARY DETERMINATION: UTILITIES BY AREAS

(Based on production 625,000 lbs. smokeless powder per 24 hrs.)

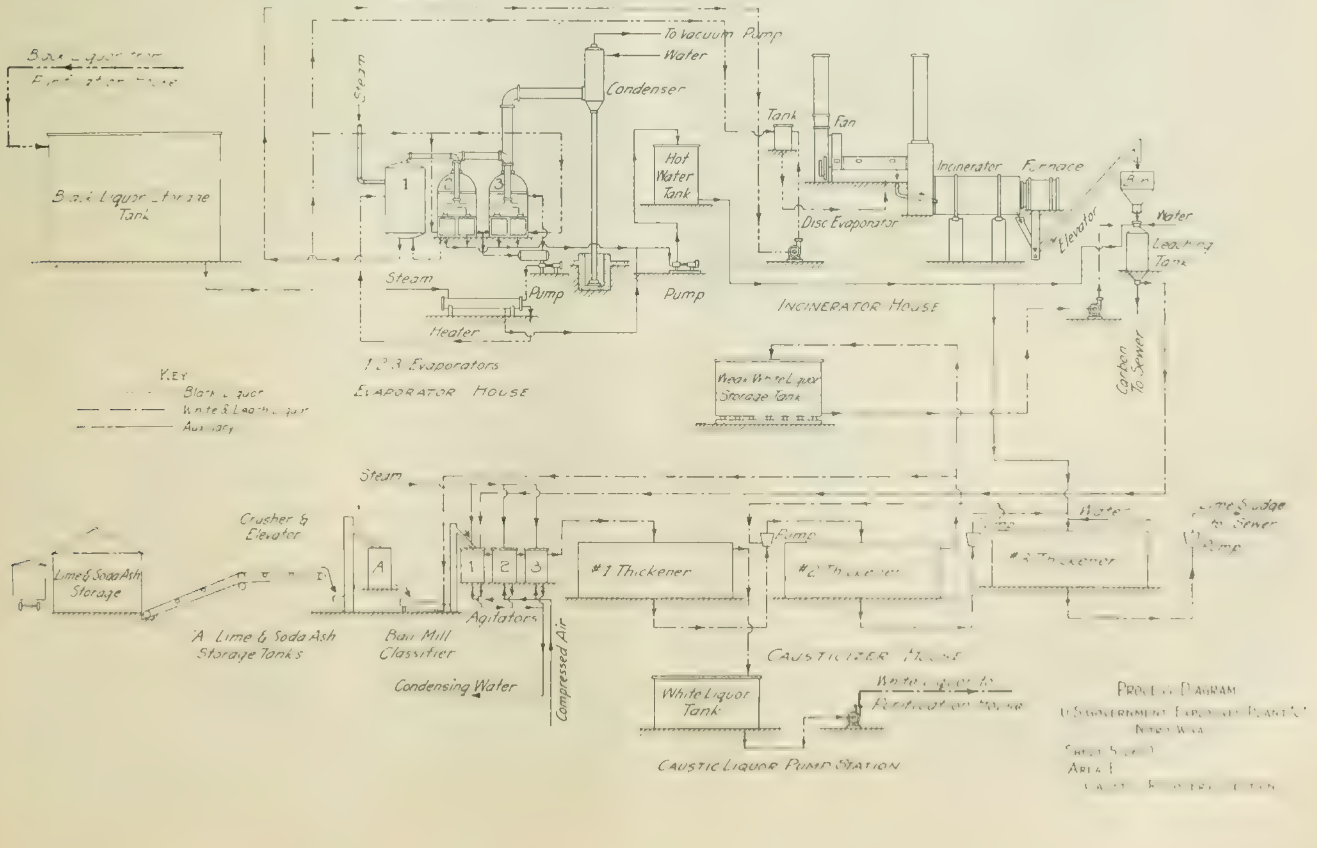
Water in gals. 24 hrs.

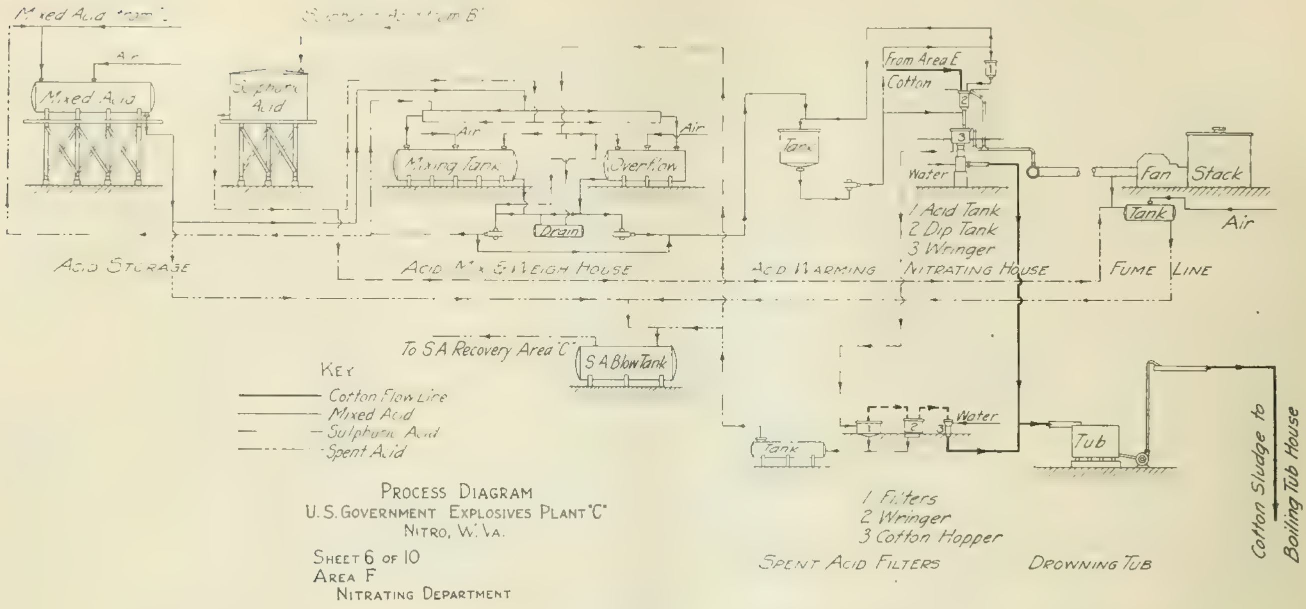
	Total Raw	Total Filtered	Total Area	Amt.[2] per Unit of Area Prod.	Amt. per Lb Smokeless Powder: Raw	Filtered	Total Area
Sulfuric Area							
Absorber buildings	1,209,600				1.94		
Lead tower	18,400				.83		
SO_2 coolers	1,728,000				2.76		
TOTAL	3,456,000	......	3,456,000	5,370[1]	5.53	...	5.53
Nitric Acid and Spent Acid Recovery Area							
Nitric acid and denitration	2,160,000	864,000			3.46	1.38	
Niter-cake flume	2,448,000	......			3.92	....	
Wash water filters	......	2,016,000			....	3.23	
TOTAL	4,608,000	2,880,000	7,488,000	13,000[2]	7.38	4.61	11.99
Raw Cotton Purification and Bleaching Area							
Purification houses	......	5,760,000			....	9.22	
Evaporation building	10,080,000	......			16.10	....	
TOTAL	10,080,000	5,760,000	15,840,000	63.300[3]	16.10	9.22	25.32
Nitration, Pulping and Purification Area							
Drowning sump houses		6,480,000				10.38	
Pulping houses		1,800,000				2.88	
Poacher		7,200,000				11.50	
TOTAL	......	15,480,000	15,480,000	24.76	....	24.76	24.76
Colloiding Area							
Ether and alcohol houses	7,200,000	......	7,200,000	11.50	11.50	....	11.50
Drying Area							
Refrigeration plant	......	4,320,000			....	6.91	
Water dry houses	......	216,000			....	0.35	
TOTAL	......	4,536,000	4,536,000	7.26	....	7.26	7.26
Power Area							
Turbo-generator and auxiliary	4,830,000	......			7.73	....	
Service and cooling water	......	2,160,000	6,046,000		....	0.34	
TOTAL	4,830,000	2,160,000	5,046,000		7.73	0.34	8.07
Domestic and General Service Area							
	......	3,240,000	3,240,000	100[4]		5.18	5.18
TOTALS	30,174,000	32,112,000	62,286,000		48.24	51.37	49.61

[1] Based on 644 tons 100 per cent H_2SO_4 per 24 hrs.
[2] Based on 576 tons 100 per cent HNO_3 per 24 hrs.
[3] Based on 250 tons purified cotton per 24 hrs.
[4] Based on 32,400 inhabitants.

GENERAL POLICY OF CONSTRUCTION

The operation of the plant was undertaken by one of the large powder companies. It was necessary that this company start operations before the construction of the plant was completed. As may be readily seen, this introduced serious additional complications. It soon became evident that the system employed for directing the work was rapidly becoming ineffective. To correct this difficulty, an executive committee was formed composed of representatives of the director, contractor, architect, and the operating company. This executive committee had final and full jurisdiction over every matter pertaining to design, construction, and operation.





In general the construction proceeded in the same order as the flow of product. For the purpose of speedy construction it was necessary to construct temporary sewers, tracks, and water lines. These were so constructed as not to interfere with the permanent systems afterward put in.

Team work, coöperation and harmonious action between the various organizations were of primary importance. A change in design or delay in construction not only affected the immediate organization or portion of the plant concerned, but almost in every case had a bearing on every other part of the work. This effect was much more serious in construction than it was in the design, but the elimination of all difficulties of this character was accomplished through the committee mentioned above. This committee met daily and discussed and settled all questions involving priority of work, change in design, etc. The first order of business of the committee was to report on the progress of each phase of the construction. Any construction which was behind was reported to the proper executive whose duty and authority it was to see that sufficient men and materials were diverted to this work to enable it to regain its place in the general procession. The second order of business was to report on similar work which had been assigned at a previous meeting. Questions of change in design were discussed at these meetings in the same way. For example, the construction manager and designing engineers might develop a design which would be excellent from the construction standpoint but which in the experience of the operators might be unworkable or which might change the requirements of one of the utilities for a particular section.

In this committee the effect of the change was considered from each standpoint and the resultant design thus embodied all viewpoints capable of support by sound reasoning. Furthermore, any change in the unit requirements was immediately apparent and the interested departments received instant notification.

It is worthy of note not only that the executive committee immediately corrected the difficulties that had arisen by reason of the injection of the operating organization, but also that such a complete change in method of control of a big engineering undertaking could be made practically over night without in any way disrupting the organizations concerned. While the director of course had authority to make final decisions in any case, never once after the formation of the executive committee was he called upon to render a decision by reason of the inability of the committee to agree.

The duties of the director's staff were to supply all the

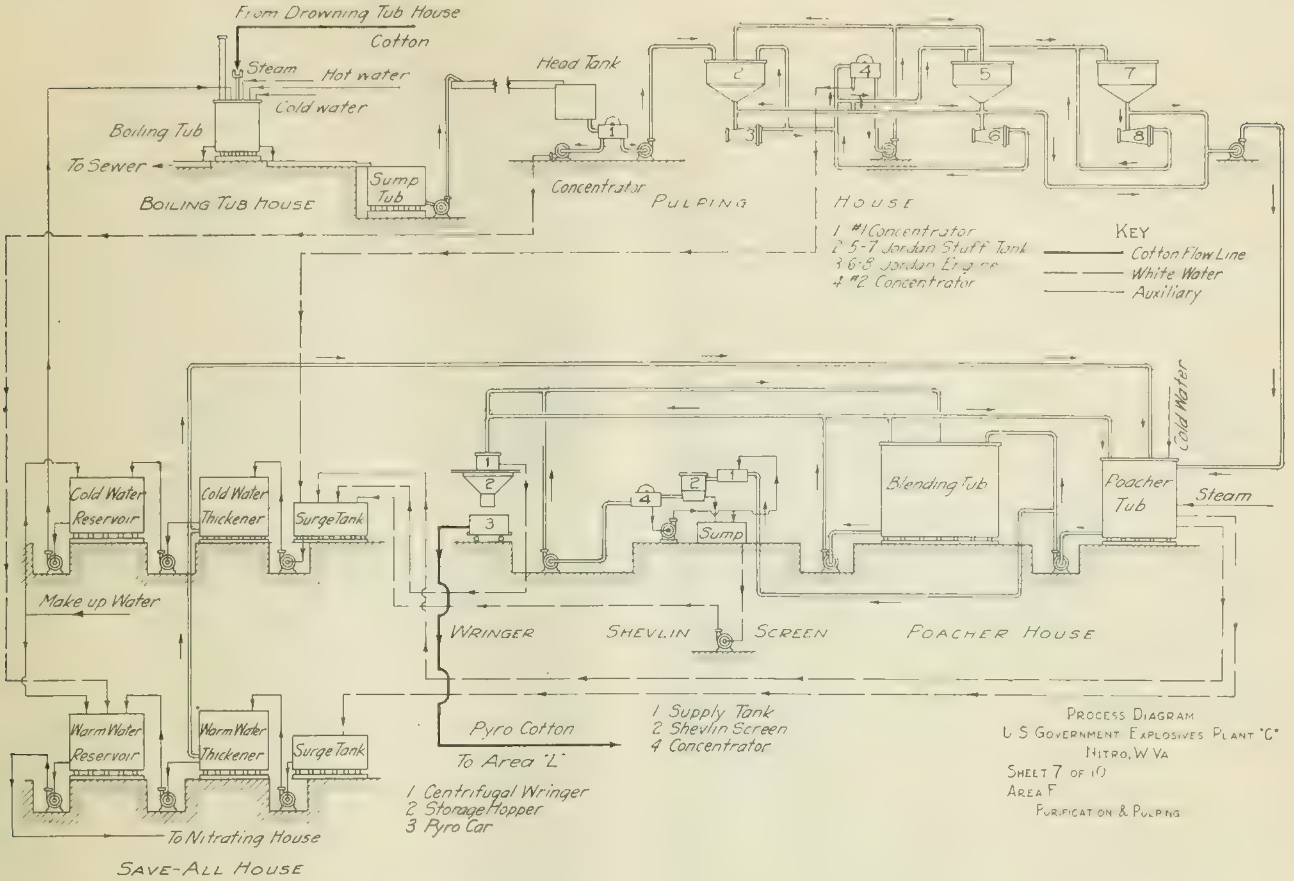
TABLE III—UNIT SYSTEM OF PRELIMINARY DETERMINATION: UTILITIES BY AREAS

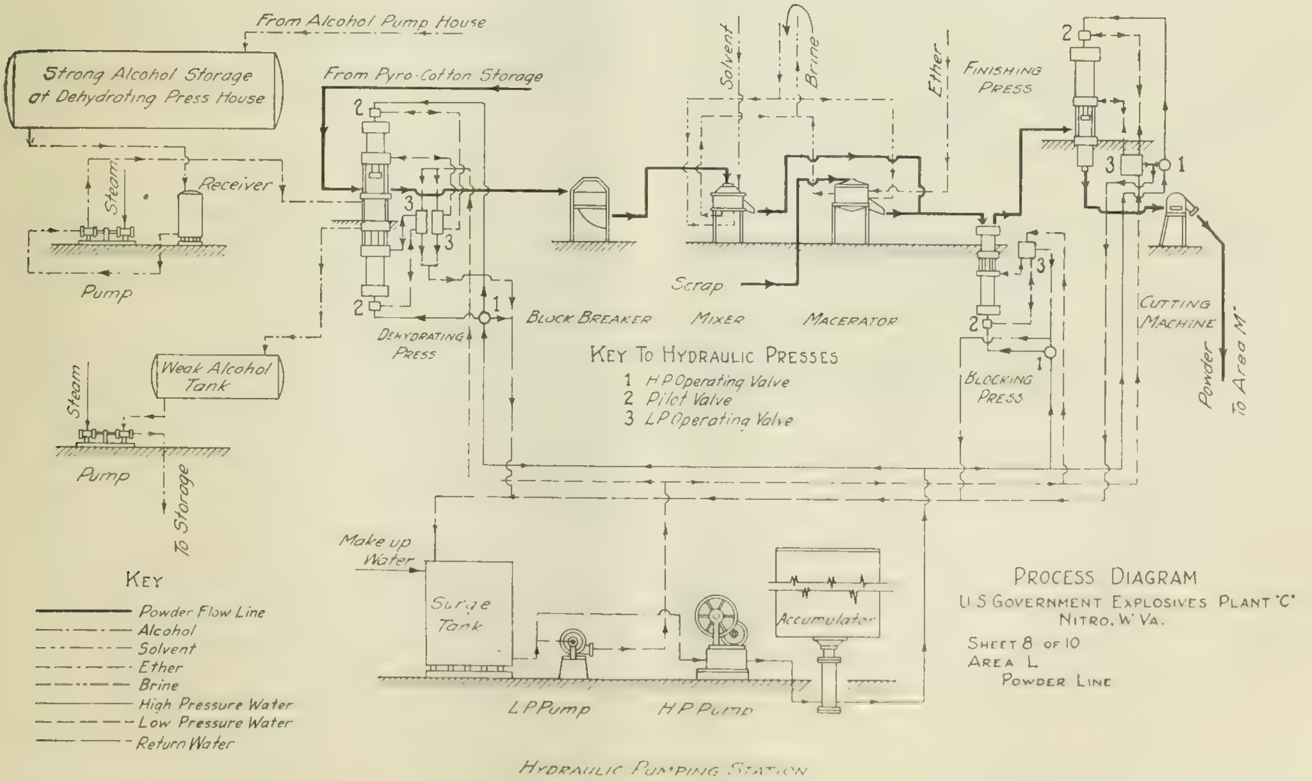
(Based on production 625,000 lbs. smokeless powder per 24 hrs.)

	STEAM IN LBS. HR.			ELECTRICITY IN KVA MAX.			GAS IN CU. FT. 24 HRS.		
	Total	Per Unit of Area Prod.	Per Lb. Smokeless	Total	Per Unit of Area Prod.	Per Lb. Smokeless	Total	Per Unit of Area Prod.	Per Lb Smokeless
Sulfuric area	2,840	4.37[1]	0.0046	2,215	3.40[1]	0.0036	3,660,000	5,680[1]	5.85
Nitric acid and spent recovery area	41,446	71.80[2]	0.0662	806	1.4[2]	0.0013	3,836,000	6,660[2]	6.13
Raw cotton purification and bleaching area	305,120	1220.0[3]	0.4870	2,459	9.8[3]	0.0039	....	....	....
Nitration pulping and purification area	621,000	0.994	0.9940	4,410	0.0071	0.0071	....	....	....
Colloiding area	88,355	0.141	0.1410	4,946	0.0079	0.0079	....	....	....
Drying area	245,000	0.393	0.3930	1,374	0.0022	0.0022	....	....	....
Power area	280,000	....	0.4480	282	0.0005	0.0005	....	....	....
Mechanical area	7,060	....	0.0113	325	0.0005	0.0005	....	....	....
Domestic and general service areas[5]	89,487	2.8[4]	0.1430	3,067	0.095[4]	0.0049	1,500,000	46.3[4]	2.40
TOTALS	1,680,308	....	2.6881	19,884	....	0.0319	8,996,000	....	14.38

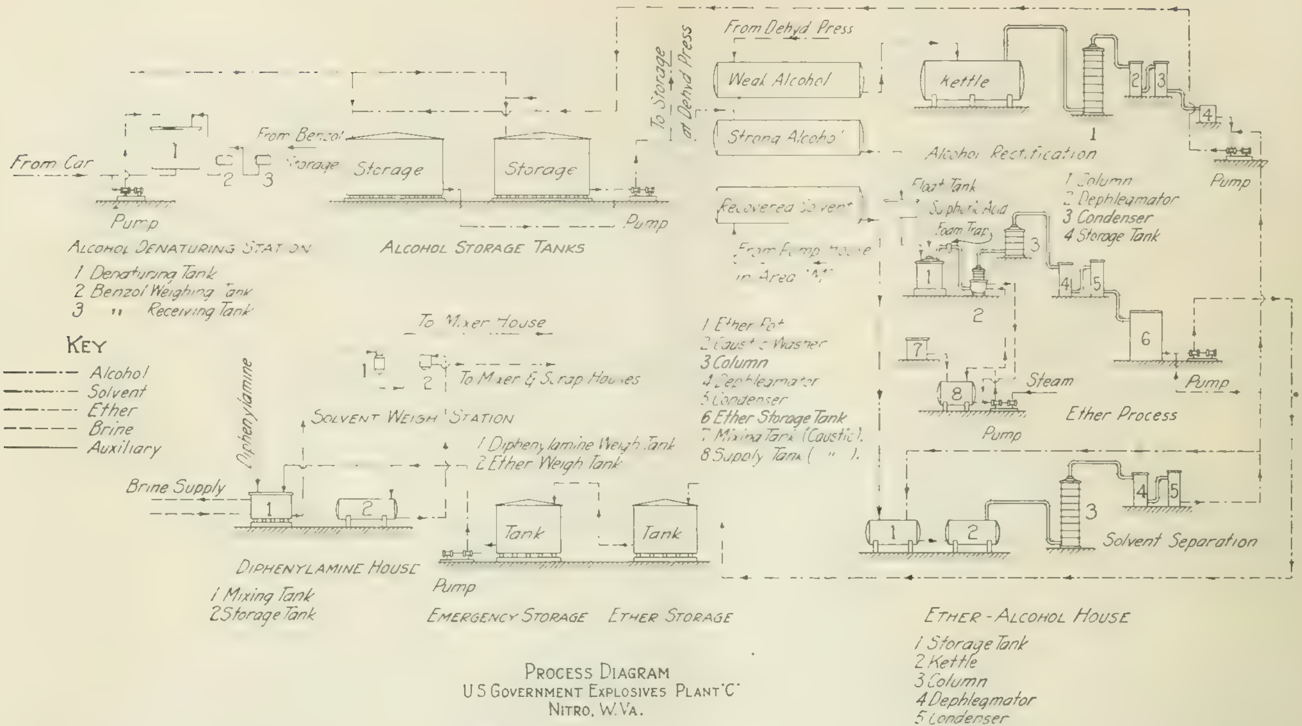
[1], [2], [3], [4] See footnotes, Table II.

[5] 6,920 lbs. from boiler plant
82,567 lbs. from isolated heating plants
89,487 lbs.





technical information necessary for the design. This was done by dividing the work into about twenty subdivisions; the work of each subdivision was correlated by a small group of men in the director's staff. The same subdivisions were used in the contractor's division and in the architect's division. Each subdivision of all the general divisions was in charge of an experienced man. There were created small committees of four men each, representing all of the activities of any department, and the work of these men was finally correlated through the main executive committee.



PROCESS DIAGRAM
U S GOVERNMENT EXPLOSIVES PLANT "C"
NITRO, W. VA.
SHEET 9 OF 10
AREA L
ETHER ALCOHOL PROCESS

The above is a very general outline of the organization used to build the plant and the methods by which the work was accomplished. The magnitude of the problem and the success which attended its solution can best be attested by a brief summary of what was accomplished.

The plant site occupies 1772.10 acres of which 1209.57 acres or 68 per cent were available for plant buildings or housing.

In designing and constructing the plant 4325 drawings were made and 4235 specifications prepared. Over 20,000 purchase orders were placed, covering items of plant equipment and material, and 37,236 cars of material were received at the plant. The accounting department handled over 58,000 invoices under 20,600 vouchers, paid 45,000 freight, express, steamboat, and demurrage bills, made 4000 adjustment claims, and sent out over 45,000 letters and communications.

The principal materials used in the construction of the plant were as follows:

MATERIAL	QUANTITY	UNITS	CARS
Ballast	......	....	2852
Brick (all kinds)	30,000,000	....	2225
Cement	335,448	Bbls.	1532
Stone	435,067	Tons	4269
Sand	123,504	Tons	1531
Iron pipe: c.i.	9,938	Tons	1060
screw	4,486,087	Feet	
Houses, portable			2006
Lumber	110,152,000	Bd. ft.	4339
Lath	4,170,900	....	....

A total of 86,547 men were enrolled. The average field force employed was 9048. The average turnover was 9.56 or 74 per cent per month, and the average length of service was 40 days. The maximum number on the payroll was 18,828, and the payroll for that week was $852,343.83. All labor on an hourly basis was paid time and one-half for overtime and double time for Sundays. The working day was 10 hrs., but the men were paid on an 8-hr. basis, or for 11 hrs.

The labor was divided into 9233 skilled, 5959 unskilled, and 3536 all others. On November 11, 1918, the operating force numbered 4550 of which 250 were women.

Fatal Explosion and Fire

A fatal explosion and fire occurred at the plant of E. L. Gowdy Co., Brockton, Mass., January 19, 1922. The business of the company consists of impregnating wool felt with shellac and rosin dissolved in denatured alcohol. The felt thus treated is dried by heat and cut into pieces for use in the box toes of shoes.

In the process, the felt is fed over dehydrating cylinders into the saturating solution, in which it is completely immersed, then through a wringer into the main oven, built of galvanized iron. In the oven it passes over a stack of four unheated galvanized sheet iron cylinders, through a partition into a second compartment, over eight steam-heated cylinders, and out over eighteen heated cylinders at the rear of the oven, to a bench where it is cut into sheets. Exhaust fans attached to the oven remove the alcohol vapors, which are recovered by passing through an outside condenser. The oven cylinders and those at the rear are wrapped in paper to prevent the solution from sticking to the iron. This paper gradually becomes coated with dried shellac and rosin, and is removed every few days.

The explosion occurred in the second compartment of the oven. In the opinion of Mr. Walter L. Wedger, the State official who investigated the explosion, it was caused by a spark of static electricity, generated in dangerous intensity on the shellac-coated paper on the cylinders in the second compartment of the oven, caused by the passage of the felt over the shellac-coated surface. Regardless of the fact that the iron work of the oven was grounded electrically, it will be seen that the shellac-coated paper formed an insulated reservoir or gap, across which the generated current had to jump before it could reach the grounded iron work, rendering such grounding useless.

In the opinion of Mr. Wedger, the solution of the difficulty lies in the exclusive use of a noninflammable solvent for saturating the felt.

A New Method of Color Measurement for Oils[1,2]

By **Leon W. Parsons**[3] and **Robert E. Wilson**[4]

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This article discusses the need for and the development of a new and consistent method for the rapid and accurate measurement of the true color of practically all petroleum oils, from the lightest to the darkest. By true color is meant a figure proportional to the amount of coloring matter present in the oil.

The Lovibond method is shown to be very unsatisfactory, chiefly for the following reasons: (a) As a result of the wide separation of the light squares in the instrument and the "off" tint for certain colors it is impossible to obtain an accurate and reproducible measure of the color; (b) it necessitates the use of kerosene solutions in order to match any oil above 500 color. This process is time-consuming and necessitates an entirely different color scale bearing no simple relationship to the original Lovibond scale; (c) the most serious objection to the method is that the Lovibond scale is not "true," i. e., its colors are not additive; hence the Lovibond color is not proportional to the actual amount of coloring matter in the oil, and hence the Lovibond colors of mixed oils are not additive.

The fundamental laws of color measurement are presented in detail, with data regarding their application to the problem in hand.

The reasons for the development of each step in the new method are described in detail.

The new method gives a rapid and accurate procedure for determining the true color of practically the whole range of petroleum oils from 1 to 5000 color, by making use of a single standard. The Duboscq colorimeter is used and the depth of standard color solution necessary to match a given layer of the unknown oil is determined. The thickness of the unknown oil varies from a very thin, accurately measured film for the darkest oils to a 10-cm. layer for the lightest oils.

The advantages of a true color scale are:

(a)—It makes possible the determination of the actual amount of coloring matter removed by fuller's earth under definite conditions, a quantity absolutely fundamental in an investigation of oil decolorization.

(b)—By a study of the effluent color curve (Plate X) it is possible to determine the average color of a batch of filtered oil from the effluent color at any given time and the weight of oil filtered up to that time.

(c)—The true color of mixed diluted oils may be predicted accurately from the true color of the original oils used, information which is of fundamental importance in oil blending.

A plot is presented (Plate VIII) showing the deviations of the Lovibond from the true color scale. By means of this plot it is possible to convert Lovibond color to true color readings and thus secure the above-mentioned advantages of a true color scale, even if the Lovibond system should remain the basis for routine work.

In view of the many advantages of the new method, and its successful use for over a year in this laboratory, it is recommended for adoption not only for research where it is absolutely indispensable, but also for plant control. Specific directions are given for its use in the laboratory.

By a modification of the standard used, this method has been applied with quite satisfactory results in the investigation of other problems, for example, the colors of sugar solutions, of certain vegetable oils, of dyestuff solutions, and of black liquor from soda cooks.

SCOPE OF INVESTIGATION

THIS article describes the results of an extensive investigation of practical methods of color measurement for petroleum oils, which was carried out in preparation for a fundamental study of decolorization processes. The work was financed by the Vacuum Oil Company, and was carried out in coöperation with their Rochester laboratory. It is published with their kind permission.

While practically all the fundamental experimental work has been carried out on petroleum oils, the same principles have been applied with quite satisfactory results in certain other fields of investigation in this Laboratory, notably, the colors of sugar solutions, of certain vegetable oils, of dyestuff solutions, and of black liquor from soda cooks. It should, therefore, be of considerable interest outside the field of petroleum oils.

There are at the present time three generally recognized methods of measuring the color of petroleum oils—the National Petroleum Association method, the Saybolt chromometer, and the Lovibond method. The National Petroleum Association method consists of viewing the oil in a 4-oz. bottle and comparing it with a set of six or seven arbitrarily chosen colors. With the Saybolt chromometer, a rough comparison is made through two vertical glass tubes, matching the color of an unknown oil with that of a colored disk, the color standard being comparable to the color of potassium dichromate solutions. While both of these methods are adequate for many trade purposes, they are obviously of little value for accurate measurements or for research work on decolorization problems.

The Lovibond method is a much more ambitious attempt to establish a color scale suitable for accurate measurements. It consists essentially in comparing the color of a cell (usually 0.25 in. thick) of the oil with successive members of a series of colored glasses which have been made to conform to an arbitrary color standard. In making these comparisons the general practice in the petroleum industry is to use a series of amber-colored glasses, although occasionally use is made of other members of the complete series of glasses, which includes the following colors—yellow, amber, red, and blue—matching the color as closely as possible by the most suitable combination of these four. The comparison with the oil in the cell is made in a rather crude manner by adding or taking away glasses until the two squares of color which are separated by a wide black partition appear to match.

It was the intention of this Laboratory to adopt the Lovibond color scale in their investigations on the decolorization of oils, but a few weeks' experience with the method indicated that it was very poorly adapted for the purpose in hand, especially for measuring the color of the unfiltered or partially decolorized cylinder stocks.

The principal defects in the Lovibond method are as follows:

1—It is difficult, especially for an inexperienced operator, to get accurate matches even in the best part of the scale because of the wide separation of the two squares of light. This difficulty could of course be obviated by a suitable optical device

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[1] Presented in abstract before the Section of Petroleum Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Contribution No. 43 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

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so arranged as to give a split field with no marked line of division between the two color areas.

2—While the glasses match the color of the oils fairly well for colors between 3 or 4 and 200, they give a distinctly "off" tint for colors below or above this range, and especially for colors above 400°, where it is almost impossible to get a satisfactory match. Readings in this vicinity frequently vary by as much as 25° for the same observer on the same oil.

3—For colors above 400° Lovibond it is customary to use 5 per cent solutions of the oil in kerosene. This requires more time and necessitates an entirely different color scale which bears no simple relationship to the original Lovibond scale. Furthermore, it is applicable only to oils whose original color does not exceed 2000, and it cannot be employed successfully for the unfiltered cylinder stocks. If higher dilutions are used it is difficult and time-consuming to make them accurately.

4—The most serious objection to the Lovibond method is that its scale is not "true," *i. e.*, its colors are not additive. For example, a 10 per cent solution of a 400° oil in kerosene does not give a 40 color, as might be expected, but instead a color in the neighborhood of 78. Similarly a mixture of 50 parts of a 100° oil and 50 of a 400° oil gives approximately a color of 283° instead of 250° as would be the case if a true color scale were used. It is obvious from this that the Lovibond color, as measured by the standard glasses, is not proportional to the amount of coloring matter in the oil, on account of a faulty scale used in making the standard glasses. This fact is an almost insuperable objection to the use of such a scale in any fundamental investigation of the laws governing decolorization.

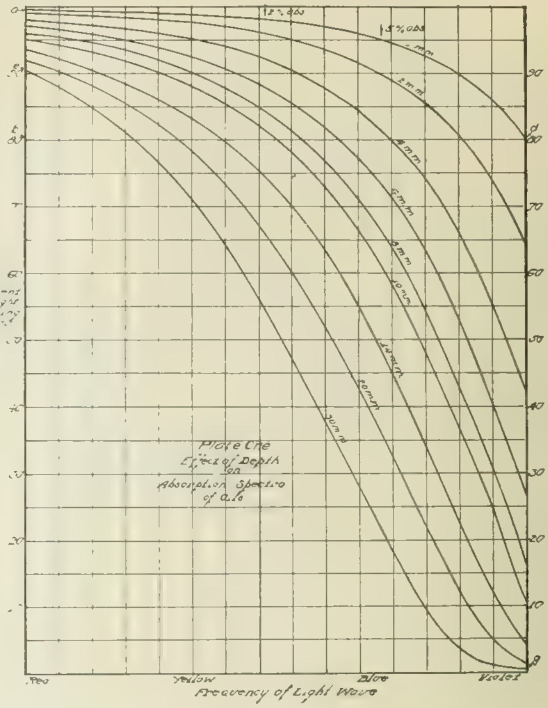
In view of the unsatisfactory nature of the existing technical methods of color measurement it soon appeared necessary to develop a new and consistent method of color measurement which would cover the whole range of lubricating oils from the original very dark oils down to the lightest filtrates, and, if possible, give a "true" or strictly additive color scale over this range. It was furthermore essential that the method be both rapid and accurate, in view of the number of determinations which must be made, and the importance of the conclusions to be drawn.

Several modified or new procedures were later tried out, but eventually the one hereinafter described was found to be the most satisfactory for the whole range of darker oils in which this Laboratory was especially interested.

Fundamental Principles of Color Measurement

Before proceeding to any detailed discussion of the best methods for determining the color of oils, it is necessary to discuss briefly the fundamental physical principles which are applicable to the problem. To the human eye there appears to be no evidence of any simple law indicating how the color of a solution changes with increased thickness; even a casual observer realizes that certain light yellow solutions when viewed through a deep layer may give simply a darker but very pure yellow, whereas others quickly shift to orange and red on the one hand, or green on the other, merely by increasing the depth through which the white light passes before reaching the eye. This apparently complicated phenomenon is due merely to the fact that the eye is not able to distinguish separately light of different wave lengths, but integrates the effect of the spectrum as a whole in such a way as to give a single sensation.

When, however, absorption of monochromatic light, or light of a single wave length, is studied, a very simple law is found to hold, namely, that the amount of light absorbed in passing through a given thickness of a homogeneous material is a constant percentage of the light which enters that section. Thus, if one centimeter of a given oil absorbs 20 per cent of a certain wave length of blue light, the second centimeter will absorb, not an equal amount, but 20 per cent of the 80 per cent which enters it; in other words, 16 per cent of the original light. Similarly, the third centimeter will absorb 20 per cent of 64 per cent, or 12.8 per cent of this particular color. The mathematical expression of this fact is that $\log x = kl$, where x is the fraction of light remaining unabsorbed after passing through thickness l, k being a constant depending upon the properties of the original material.



It is not possible, of course, to predict how much of any other color, such as yellow or red, would be absorbed by one centimeter thickness, since this depends entirely upon its individual characteristics. The important thing is, however, that if the complete light absorption curve is known for any one thickness of the liquid, the curve for any other thickness can be calculated readily and accurately.

In the case of colored solutions, the effect of the *concentration* of the coloring matter on the absorption of light is not known with any such mathematical certainty. Beer's Law states that the effect of doubling the concentration of coloring matter is the same as that of doubling the thickness. Most of the literature on the subject, however, is devoted to showing that, as a matter of fact, Beer's Law does not hold at all accurately for most cases of colored solutions. A perusal of this literature indicates, however, that the deviations from Beer's Law are usually not large except in the case of aqueous solutions of ionized materials, where factors such as the hydration of the ions and the degree of ionization unquestionably have a serious disturbing influence. In the case of organic coloring matter in organic solvents, it is fairly well established that Beer's Law holds with reasonable degree of accuracy in most cases, though this cannot be assumed safely in the absence of definite data, however convenient it might be in working out a satisfactory method of color measurement. It is obvious, therefore, that as a foundation for the work in hand it is necessary to determine the type of light absorption curve for lubricating oils, and to find out whether or not Beer's Law applies over the range of concentrations which would be encountered in practice.

Determination of Fundamental Properties of Coloring Matter in Lubricating Oils

In undertaking a preliminary investigation of the coloring matter present in oils, the first and most important characteristic which was discovered was that practically all paraffin base oils from very pale yellow spindle oils down to extremely dark-colored, unfiltered, cylinder stocks had essentially the *same* light absorption curve, providing the heavier oils were diluted down or viewed through films which were sufficiently thin. Even dark oils which differed markedly in their general appearance and appeared a fluorescent purple, green, or red, when viewed by reflected light, gave almost identical colors when viewed through sufficiently thin films or in dilute solutions, and it was possible to secure very satisfactory color matches by such means between widely varying original oils.

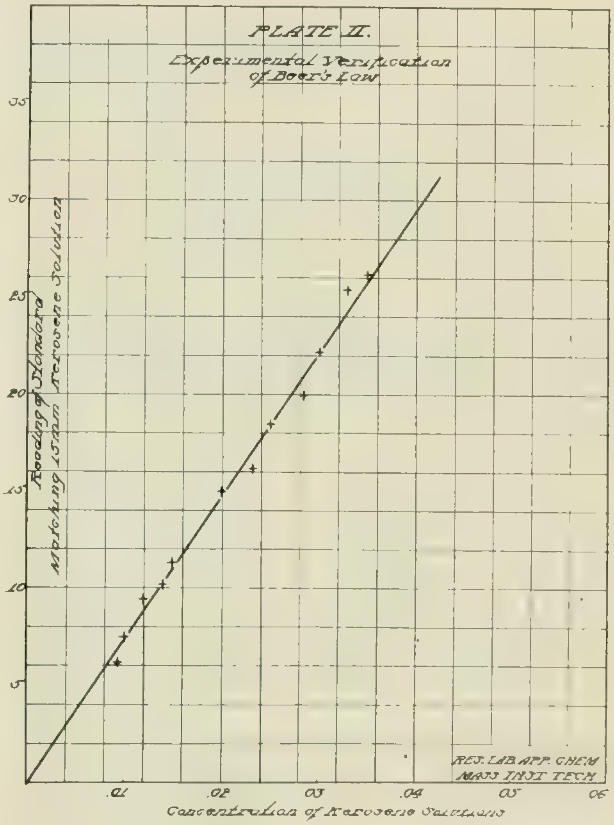
Plate I, Curve *ad*, represents a rough approximation of the light absorption curve for a 1-mm. thickness of a fairly light-colored lubricating oil. It is realized that if extremely accurate absorption spectra were obtained—for example, with a spectrophotometer—these curves would show some irregularities, but in general the curves which are plotted represent the type of absorption spectrum obtained with a good spectroscope. It will be noted that the absorption in the red is extremely small, while the absorption in the blue and violet is very high. Using the above-mentioned law it is possible to calculate the light absorption curve for other thicknesses of the oils as indicated on Plate I. Curve *eg*, for example, indicates the light absorbed by a 30-mm. layer of the same oil, but since all oils give the same general type of light absorption curve, if used in fairly thin layers, it also represents approximately the light absorption curve for 1-mm. thickness of an oil which contains roughly (or exactly if Beer's Law holds) thirty times as much coloring matter per unit volume. By inspection of this interesting series of curves, it is possible to obtain a clear picture of the series of changes which occur in the apparent color of the oil as seen by the eye.

Taking an absorption curve for 1-mm. thickness, it will be noted that the light represented by the area below the horizontal line *bd* contains all the components of light in the correct proportion to give white light. But the part above the line and below the absorption curve *ad* contains a considerable deficiency in the blue end of the spectrum. The center of gravity of this area is, therefore, in the greenish yellow part of the curve, and the eye, which must average up the combined effect of 80 per cent white light plus 20 per cent colored, records the sensation of a pale, slightly greenish yellow color. As the thickness of the layer (or concentration of color) increases and we proceed to lower and lower absorption curves, it is obvious that less and less white light is coming through. This makes the colors appear much darker and furthermore the absorption curves are becoming steeper and the center of gravity is more and more displaced towards the orange-red end of the spectrum. The visual sensation given by a line such as *eg* would, therefore, be a very dark orange-red color. Intermediate absorption curves will, of course, give an intermediate sensation.

It will be seen thus that starting with a single light absorption curve it is possible to account for all the observed colors, ranging from the very pale lemon-yellow to a very dark orange-red or red-brown. The green or purple tinges which show up by reflected light are not apparent when viewed by transmitted light.

It is furthermore obvious from an inspection of the curves that the best matches and the most accurate color measurements can be obtained in an intermediate range only. The colors of very light oils cannot be measured accurately because there is so much white light coming through, while the sensitivity of any match drops off very rapidly as the absorption curves approach the bottom of Plate I, as may be observed by noting the much closer spacing of lines for a given increase in color. Small differences in the shape of the curves also make trouble in thick layers. Any satisfactory system of color measurement must, therefore, plan to bring the heavier oils to this range of color where accurate measurement is possible, either by dilution with a solvent or by using varying thicknesses of layer down to a very thin but accurately measured film for the heavier oils.

It was also necessary to determine the validity of Beer's Law for the coloring matter in oils. This was done by two different methods in two widely different ranges of color. In the first case a standard 10 per cent solution of dark-colored heavy oil in kerosene was made up. This solution was carefully diluted further with kerosene to give concentrations of heavy oil varying from 1 to 4 per cent, and a constant depth (15 mm.) of these solutions was compared with a single standard solution (containing 2 per cent oil) whose depth was varied as necessary to get a precise color match. This depth was measured accurately in a Duboscq colorimeter, operated as described later. The results obtained on this series of samples are shown graphically on Plate II, where it may be noted that, as Beer's Law would require, the depth of standard solution required to match the constant depth of variable solutions was directly proportional (within the limit of error) to the concentration of oil in the variable solutions.



When the film method of measuring heavy oils was finally perfected, another verification of Beer's Law was obtained by working with very dark-colored oils. The procedure was as follows: Heavy oil, A, would be compared in a thin film, whose thickness was accurately known, and matched against a certain depth of standard solution; Oil B, with a widely differing color, would also be matched in the same way. These two oils would then be mixed together in exactly equal proportion. If Beer's Law holds, the depth of standard required to match this mixture should be the arithmetic mean of the two previous readings, and this was found to be the case within the limit of experimental error. Repeated verification of Beer's Law has been obtained in the laboratory by comparing colors of mixed oils on a small scale, and in the plant by blending larger quantities of oils, in some cases as high as 8000 gal.

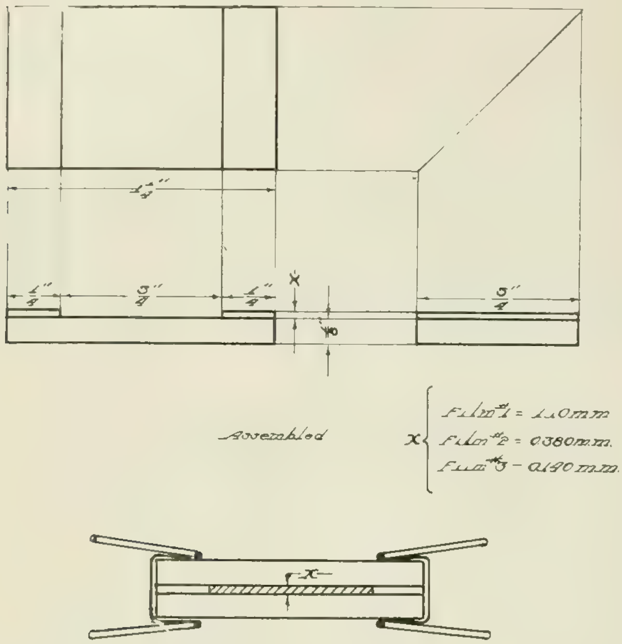


Plate III—Detail of Film Spacers

Table 1 indicates results obtained on comparing the color of mixed oils with the calculated value as obtained from the true color[5] of the separate oils used and the weight of oil taken. It will be observed that there is a very close agreement between calculated and determined color.

Table 1—Calculated and Determined Color of Mixed Oils

True Color and Per cent by Weight of Oils Used	Calculated True Color of Mixture	Measured True Color of Mixture
50% of oil (T. C. = 1790) 50% of oil (T. C. = 1400)	1595	1550
50% of oil (T. C. = 2420) 50% of oil (T. C. = 1400)	1910	1900
50% of oil (T. C. = 3200) 50% of oil (T. C. = 1400)	2300	2280
28.8% of oil (T. C. = 490) 71.2% of oil (T. C. = 1760)	1390	1400
55% of oil (T. C. = 240) 45% of oil (T. C. = 1430)	775	780
49.4% of oil (T. C. = 3200) 50.6% of oil (T. C. = 240)	1700	1725

The validity of the above relationship is, therefore, clearly established.

Beer's Law has thus been shown to hold with surprising accuracy both for fairly light-colored kerosene solutions and very dark-colored heavy oils. It will be noted that in obtaining the foregoing results, the nature of the color solvent was not varied in the dilution experiments—in the first case the solution was more than 96 per cent kerosene in all cases, and in the other it was always practically 100 per cent heavy oil. Neither these results nor Beer's Law will throw any light, however, upon the effect of diluting heavy oil with a widely different organic solvent such as benzene or chloroform, or possibly even kerosene. In order to obtain some data upon this point, a series of solutions of heavy oil was made up to a concentration of exactly 2 per cent in different solvents, and the color observed.

In this comparison, the standard of reference was a 2 per cent solution of heavy oil in kerosene. The solution thus chosen was identical in nature with the regular light standard, L. S. (hereafter mentioned), used in all of our colorimetric work, differing only slightly in concentration from it. Measurements were made in the Duboscq instrument by placing the kerosene solution in one cup, and the solutions in the other. Various settings of the plunger were made and straight line relationships obtained between the readings of the standard plotted as abscissae and the readings of the other solutions plotted as ordinates. A summary of the readings of the various solutions matching a 10-mm. layer of the standard is given in Table 2. The deviation of these readings from 10 mm. is proportional to the variation in color due to the use of different solvents.

Table 2—Colorimeter Readings for Solutions of Mineral Oil in Various Solvents

Depth of Standard Used Mm.	Depth of Solution S for Match Mm.	Nature of Solvent in S
10	13.6	$CHCl_3$
10	12.4	CCl_4
10	11.2	C_6H_6
10	9.6	Gasoline

The depths of the colors in solvents widely differing in chemical nature from the oil are shown to be, in most cases, lower than those obtained in solvents similar to the heavy oil, such as kerosene and gasoline. Furthermore, the absorption curve in the chlorinated solvents was different from that of the original oil making it difficult to obtain accurate matches. It must, therefore, be concluded that, although the dilution law holds accurately as long as the solvent is not changed, it will not hold where the relative proportions of two dissimilar solvents are varied. One series of experiments were made by diluting heavy oil accurately with kerosene which indicated that, in this case, the dilution law held within 5 per cent, but by no means as accurately as Beer's Law itself, where the solvent is kept substantially constant.

Factors Involved in Selection of Method

A discussion of the various phases in the development of a satisfactory method for measuring the color of oils is indicated below.

color standard—The best color standard appeared to be a kerosene solution of heavy oil, since this gave exactly the same type of absorption spectrum as the oils themselves. This is a great advantage, for while it is possible to obtain fair matches with standards such as the Lovibond glasses, which have a distinctly different type of absorption curve, the depth of oil required to match a given glass is dependent to a very marked extent on the sensitivity of the eye of the observer to different colors and to the source of light. On the other hand, using a standard with the same type of absorption curve, it has been found experimentally that neither the observer (providing he has had a little experience) nor the source of light has any appreciable influence on the readings obtained.

It has also been found that a single kerosene solution of dark oil matches all the lubricating oils from the very lightest to the dark cylinder stocks, providing a proper thickness of the oils is selected. The "grayness" which is, in the case of some oils, superimposed on their regular color, gives practically no trouble whatever when the color measurement is made in very thin films. In some cases, however, it is more satisfactory to use a slightly different standard for oils which have a tendency toward cloudiness or grayness. This is referred to as the dark standard, D. S., and it is designed to have exactly the same *color* value as the ordinary or light standard, L. S.

Details of operation are given later under "Laboratory Directions." The standard solutions are diluted to approximately 35 Lovibond color and then standardized exactly by comparison in the colorimeter with a 50 color Lovibond glass. The latter is selected as the standard because up to

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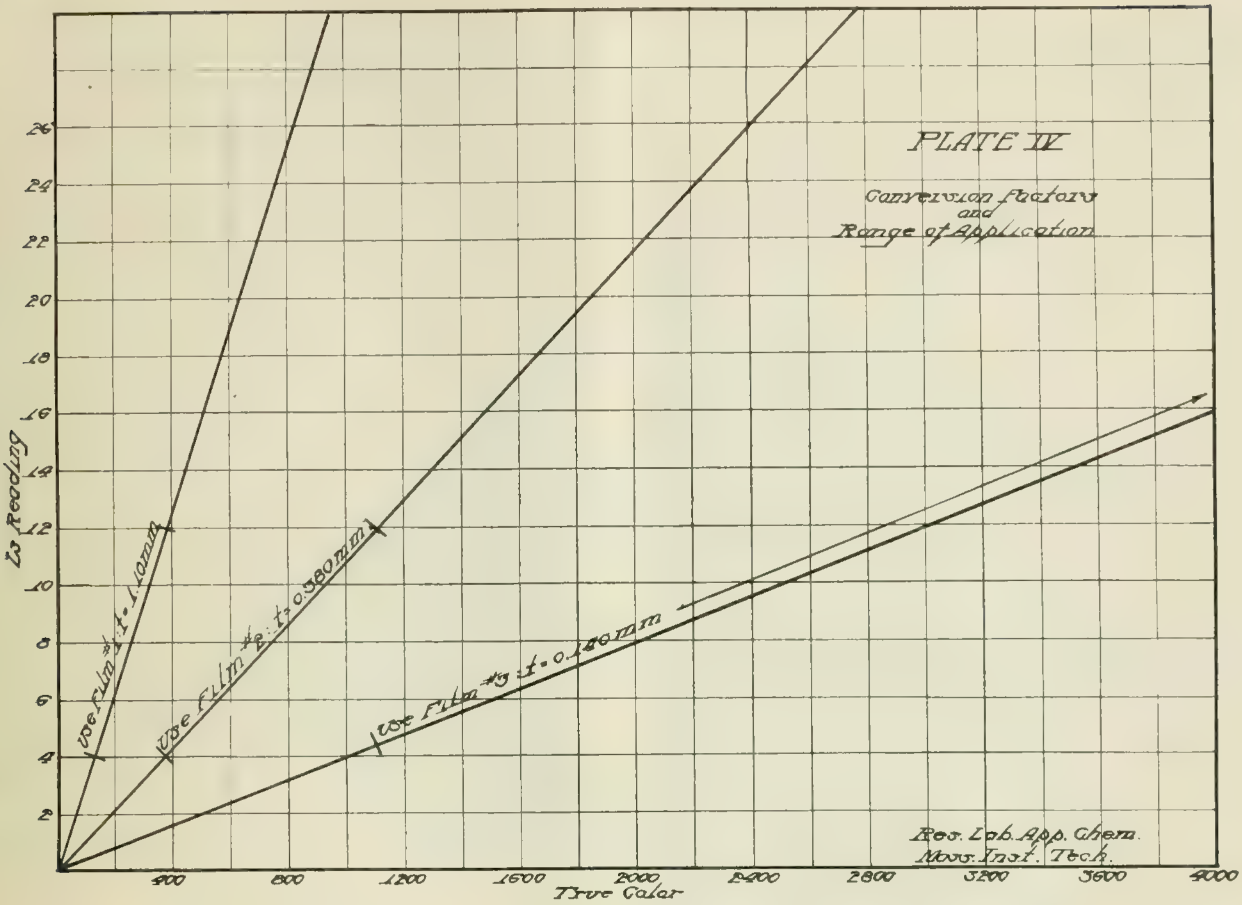
[5] The derivation of the scale used is discussed later.



this point there is no deviation between the Lovibond and True Color curve. Mixtures of different oils were examined at the Rochester laboratory in order to determine, first, whether they were more suitable for color standards, and second, their relative stability. In general it has been found that there is no advantage of these over the regular L. S. standard either regarding accuracy of matching or stability of sample.

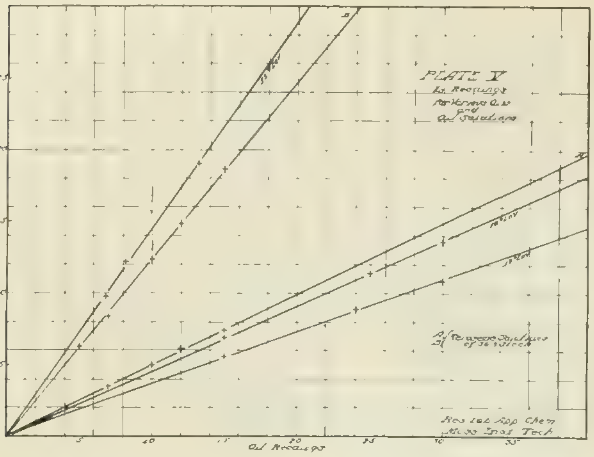
Both L. S. and D. S. standard solutions have been found to be fairly stable over a period of several weeks. Any change which does take place, however, is usually a slight increase in color and occurs within the first 2 or 3 days after preparation of the solution; consequently, it is recommended that the solutions be allowed to stand from 1 to 3 days in order to come to equilibrium before the final color value is determined. They should be protected from exposure to light and should be measured at intervals against the 50 color Lovibond glass in order to check the color value. This single Lovibond glass (which may be separately standardized) therefore becomes the permanent reference standard, while the solution is used in all measurements on oils.

MEASURING INSTRUMENT—The most suitable measuring instrument appeared to be the Duboscq type of colorimeter, since this brings the two fields in very close juxtaposition (two semicircles divided by a hair line), and permits the depth of the standard solution in one of the cups to be varied at will and measured accurately. The match can be approached slowly from both sides without interruption of light or stepwise adjustments such as are necessitated by the use of Lovibond glasses. A distinct advantage of the Duboscq over the Lovibond is that the former is easily adaptable to measuring colors of widely different types of colored solutions by merely changing the nature of a single standard. It has given extremely satisfactory results in several laboratories.

DEVELOPMENT OF THIN CELLS FOR DARK OILS—The remaining question to be determined is the best method of bringing heavier oils into the proper color range for accurate matching. As pointed out previously,[¶] this can be done either by diluting the oil with a solvent such as kerosene or by viewing it through very thin films. The former method appeared more feasible at first sight and because it was not thought practicable to measure very thin films with sufficient accuracy, considerable work was accordingly done along these lines. It was found, however, very difficult and time-consuming to measure the heavy oil accurately by diluting it with a known amount of kerosene. The method, furthermore, suffered from the uncertainty due to the use of a solvent different from the original oil.

Attention was therefore turned to the possibility of securing very thin films of oil of accurately known thickness. After several attempts the demountable type of cell shown in Plate III was developed, and with this it was found possible to reproduce thicknesses of 0.1 mm. within 1 per cent. The cell is made from two carefully prepared parallel glass plates of optical glass. On the upper surface of one plate are fastened, by means of Canada balsam, two small sections of microscope slides of a definite thickness, leaving a space in the middle of the plate to hold the film of oil. The cells may be made of any desired thickness.

It is, therefore, possible to use a single standard solution and by merely varying the thickness of the layer of the unknown oil and measuring it accurately under all circumstances, to determine the true color of any oil between No. 1 Lovibond and very dark unfiltered cylinder stocks which run above 4500 on the true color scale.



PROCEDURE FOR MEASURING COLOR—Fig. 1 shows the Duboscq colorimeter with a cup in position ready to determine the color of an oil. By moving the glass plunger the depth of liquid in the field of vision can be varied at will. A determination of the level is made by the aid of the verniers on the instrument to 0.1 mm. Using always the same standard, L. S., the thickness of the unknown oil layer may be varied at will in order to require a depth of standard sufficient to give accurate readings and yet not too deep to give a sharp match. A range of from 4 to 15 mm. of standard may be used in comparisons, but the best accuracy is obtained by adjusting the thickness of the unknown oil layer so as to keep the L. S. reading between 4 and 12.

In an actual measurement the plunger dipping into L. S. is brought very quickly to a point where the two fields observed in the eyepiece indicate an exact match between the layer of L. S. and the definite layer of unknown. This reading of the standard may be approached from both the light or dark side and a match in shade and intensity obtained very quickly and accurately. Two check readings, one from each side, are ordinarily sufficient, but for inexperienced observers five or six may well be taken and averaged, the total time necessary being very short.

For oils of true color between 3 and 200 the usual 50-mm. cups may be used for the unknown, the plunger ordinarily being set at 5, 10, 20, or 40 mm., depending on the depth of the color of the unknown oil. For oils of a true color less than 3, it is desirable to unscrew the plunger entirely and put the oil in a special cell 100 mm. deep, equipped with a glass cover which fits evenly on the top and squeezes out any excess oil. With this cup it is possible with the single standard to measure the color of oils down to 1° without any difficulty.

Oils having a color range from 200 to 4500 obviously must be measured in one of a series of thin cells such as those described above. The following three thicknesses are sufficient to cover the entire range of true color from 200 to 4500, the latter figure representing the color of the darkest oil investigated.

Cell No.	For Oils in True Color Range	Thickness of Cell
1	120 to 400	1.10 mm. ± 5%
2	400 to 1100	0.380 mm. ± 5%
3	1100 to 4500	0.140 mm. ± 5%

These limits and a conversion chart are shown graphically in Plate IV. This chart applies only to the exact dimensions of the cells as indicated above and to a standard with a true color value of 35. Special charts may be very easily constructed by individual laboratories to correspond to the cells and standard chosen.

These cells can be made readily by any expert optical worker. The exact thickness is determined by very accurate micrometric measurements on the two parallel plates and the assembled cells. By placing several drops of oil in the space between the film spacers, squeezing out the excess by pressing down the top plate, and clamping the two plates together, a film of definite thickness is obtained. It is found that the presence of oil on the spacers has no measurable effect upon the readings obtained. It was feared at the outset of the work that the use of very thin films could not be relied upon to give accurate results, but this has been definitely disproved, providing the precautions mentioned later in the "Laboratory Directions" are observed. Even with the thinnest cells the readings are found to be reproducible within 1 or 2 per cent in the hands of an experienced operator.

These films merely replace the 50-mm. cups in the Duboscq, the matches being obtained as before by varying the depth of standard. If the reading does not come between 4 to 15 mm. the wrong cell has been selected for the oil. An experienced observer can very quickly tell in which cell a given unknown oil should be placed.

CALCULATION OF RESULTS—From the foregoing discussion of the laws of light absorption, it is obvious that the true color (a figure proportional to the *amount* of coloring matter present) of an unknown oil can be calculated by the simple formula:

$$\frac{\text{Color of unknown}}{\text{Color of standard}} = \frac{\text{Depth of standard required for match}}{\text{Depth of layer of the unknown oil}}$$

Experimental Results

From a large number of data on color measurement obtained at the Rochester plant of the Vacuum Oil Company and in this Laboratory, the fundamental results have been collected and are illustrated graphically in the accompanying plates. Reference to these plates, rather than to a detailed record of various colorimeter readings, shows more clearly the relation of the Lovibond system to the true color scale and also the scope and advantages of the new method of color measurement.

VALIDITY AND SCOPE OF TRUE COLOR SCALE—The readings of L. S. for several depths of oil solutions for several light oils are shown in Plate V. It is evident that a direct proportionality exists between the depth of standard and the depth of a given oil necessary for a color match. This is true both for light oils and for kerosene solutions of heavy oils, and follows necessarily from the above-mentioned law of light absorption as a function of thickness. Such a complete

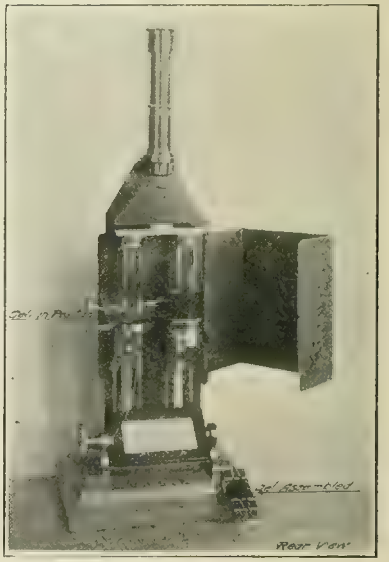
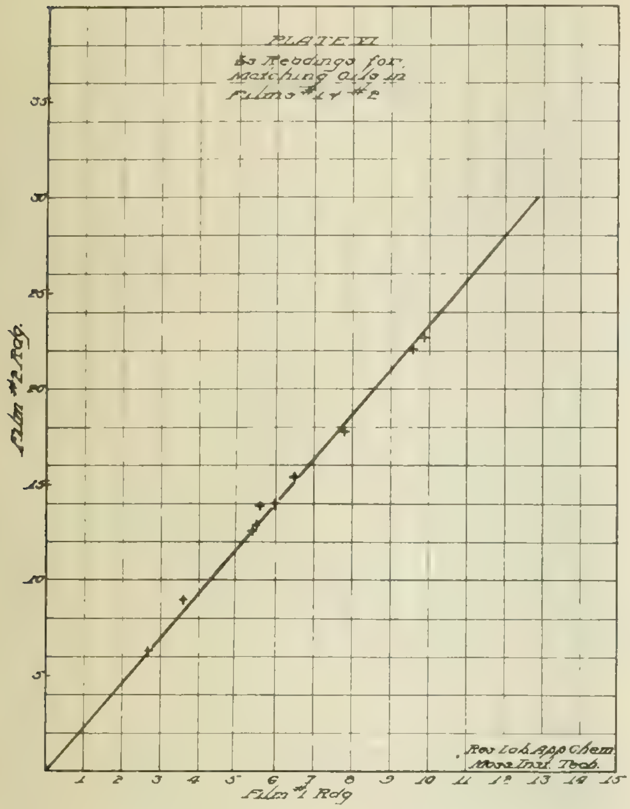


FIG 1—DUBOSCQ COLORIMETER

series of points can, of course, only be conveniently obtained when the unknown oil is in the neighborhood of 10 to 60 color and hence is in one of the regular cups so that its thickness can be varied by small stages and matched by similar variations in the depth of the standard.



From data such as are recorded in Plate II for various oils, it is also evident that a direct proportionality exists between the depth of standard and the *concentration* of color in a diluted sample of oil. This indicates definitely that a "true" color scale is obtained by this method, thanks to the fact that Beer's Law holds for the case in question. In Plates VI and VII the readings for L. S. to match different heavy oils in two different film spacers show that the L. S. readings bear a constant ratio to one another regardless of the color of the oil tested. This ratio checked within 1 per cent with the relative thicknesses of the cells as determined with a micrometer, which again shows the value of using a single color standard and merely varying its depth.

RELATION BETWEEN LOVIBOND COLOR AND "TRUE" COLOR—Plates VIII and IX show the fundamental relationship between Lovibond color and "true" color. Plate IX is an enlarged section of Plate VIII which shows the region covering the lighter oils of Lovibond color up to 150°.

In establishing this relation a large volume of data had to be accumulated. The Rochester laboratory furnished a large number of samples of oil on which the Lovibond color had been determined as accurately as possible. These were matched against the new color standard in the Duboscq colorimeter and their true color determined, thus giving the relationship between the two color scales, based, of course, upon the assumption of the Lovibond scale from 0 to 50 as the starting point of the true color scale.

As is indicated on Plates VIII and IX the points of all fall on a fairly smooth curve. The curve was further checked by comparison with data furnished by the Rochester laboratory regarding the Lovibond color readings on a number of oils and their solutions in kerosene. On merely looking at the Lovibond color values there was no consistent relation between the values obtained, but when the values were converted to the true color scale they approximated fairly closely the expected dilution laws.

By means of Plate VIII, from any Lovibond color up to 400 there may be found the corresponding "true" color. Owing to the impossibility of obtaining satisfactory Lovibond readings above 400, the upper part of the curve cannot be determined with very great accuracy. The variation of the curve from the 45° dotted line indicates the variation of the Lovibond from a "true" color series. It is evident that for the lighter oils, up to about 50° Lovibond, the two scales are identical, but from this point on the deviation gradually increases.

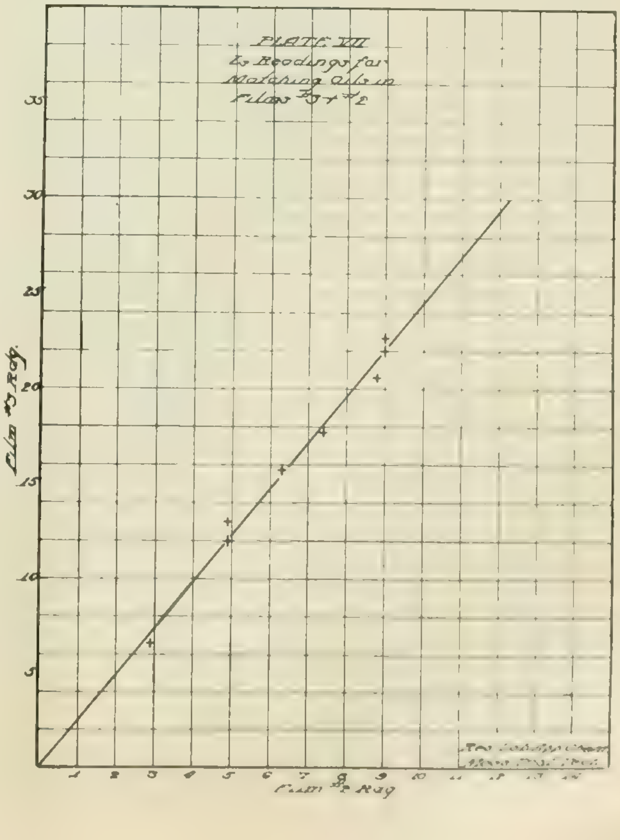
For oils above 500 color the Lovibond system required the use of a still different scale, based on the color of 5 per cent solutions which bore no simple relationship to the other scale. Using the new method the scale is a continuous straight line up to the highest colors measured.

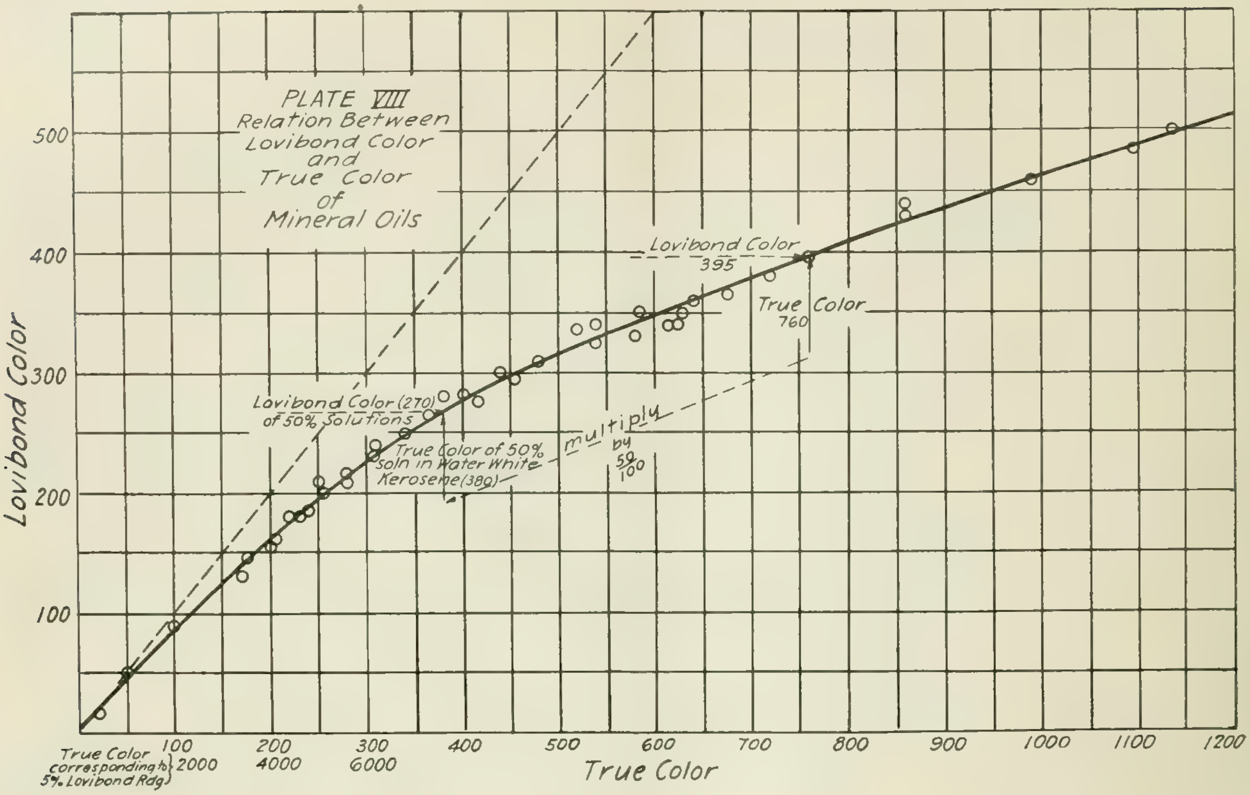
Table 3 indicates the relationship for light oils between our true color scale and other colors such as the National Petroleum Association number and the Lovibond (Series 500), the latter having been obtained from a chart submitted to the laboratory.

TABLE 3—RELATION BETWEEN TRUE COLOR AND OTHER COLOR STANDARDS

A	B	C	D
No. 1	Prime white	0.5°	0.5
1-1/2	Cream white	0.9°	0.9
2	Extra pale	7.0°	7.0
3	Lemon pale	16.0°	16.0
4	Orange pale	35.5°	35.5
5	Light red	66.0°	75
6	Red	100°	120

A = Association number. B = Association name.
C = Lovibond color (Series 500) of oil matching corresponding Association number in Column A taken in the Association apparatus.
D = True color.





PREDICTION OF THE COLOR OF MIXED OR DILUTED OILS—Much difficulty has been experienced at the plant in attempting to blend various oils, particularly the heavy oils, and predict the final color by using the Lovibond scale. If the true color value be substituted for the Lovibond the accurate determination of the color of mixed oils becomes very simple since the colors are merely the weighted average of the colors of the original oils used.

Even if the new colorimetric method should not be adopted, the relationship shown in Plates VIII and IX between Lovibond and true color will be of great value in enabling one to predict the Lovibond color of a mixed or diluted oil, knowing the amounts and the Lovibond color of the original oils. This is done by finding the true color values corresponding to each Lovibond value, calculating by simple proportionality the true color of the final mixture and then again referring to the chart to find the corresponding Lovibond color. Such results will not, of course, be as reliable as if the new method had been used throughout, because of the other inaccuracies of the Lovibond method, but the approximation will be reasonably good and should prove a great improvement over the present conditions where it is impossible to tell anything about these relationships

The dotted lines on Plate VIII show how to make the above-mentioned calculations for one case, using the Lovibond colors as a starting point. If it is desired to make such calculations on the basis of the 5 per cent solutions used in the Lovibond, it is merely necessary to keep in mind the fact that the true color of the original oil would be very nearly 20 times the true color of the 5 per cent solution, as indicated by the double scale of abscissae on Plate IX.

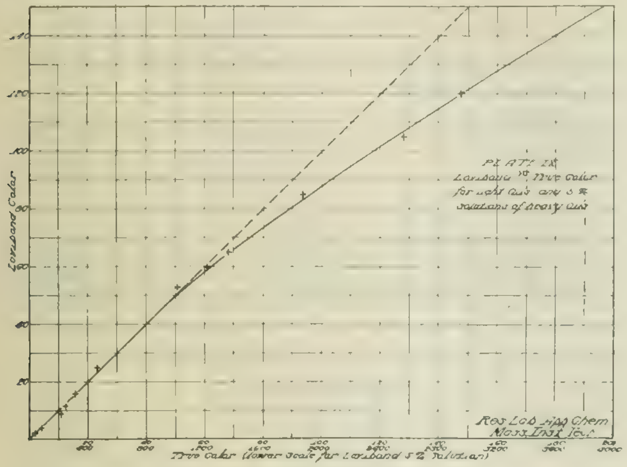
RELATION BETWEEN TOTAL COLOR OF BATCH AND EFFLUENT COLOR—Plate X shows a typical curve such as is obtained during the filtration of oil through fuller's earth. Here is plotted the true color against the weight of oil obtained from a filter, or, in other words, the color of successive samples of oil taken from the effluent stream from the filter as the filtration progresses. This curve shows graphically how much color is being left in, and removed from, the oil at any given moment. From this amount it is possible to form conclusions with regard to the efficiency of filtration. Such a plot, using Lovibond color values, would not give information about the per cent of color removed, which factor is necessary for comparing accurately decolorizing efficiencies under widely different conditions.

Furthermore, by using the new color scale, where the colors are additive, it is possible to calculate the color of the total batch up to any given time, or between any given times, merely by determining the effluent color and the weight of the batch at various times during the run.

The precise method of making the foregoing computation is illustrated in Plate X, as follows:

The line AB represents the total color of the batch at the end of x hours when the weight is ED grams. To determine this batch color in practice from the effluent color curve, the area EFCD is obtained with the aid of a planimeter and divided by the total weight at the particular time. This gives directly the batch color. The effluent color curve and the weight of oil from the filter enable one to predict the total batch color at any given time. This has been repeatedly verified both in the Laboratory and on a plant scale and is of great help in plant control. Such a calculation is not possible if the Lovibond scale is used.

RESULTS BEARING ON NATURE OF COLORING MATTER—One interesting point may be mentioned in passing, with regard to the bearing of the results obtained on the probable nature of the coloring matter in the oils. It has frequently been suggested that there might be several different coloring materials present in the oil, each of which was adsorbed to a different extent and gave a different kind of color to the oil. This might seem plausible in view of the very great difference in color between an original oil and a decolorized oil. In view of the fact, however, that a solution of the original oil can by mere dilution be made to match the same oil after it has been decolorized to any given extent, it is apparent that if there are two coloring matters in the oil they either have almost identically the same color absorption in different parts of the spectrum, which is improbable, or else they are adsorbed to the same relative extent by the fuller's earth. In the latter case the coloring matter might as well for all practical purposes be considered as one single material.



The only possible exception to this statement is in the case of the so-called "grayness" observed in the darker oils which is, however, at best a small factor and is probably due to partly solidified paraffin or to fairly large colloidal particles of carbonaceous material. Certain oils from special districts have a purplish or other unusual tint when viewed in thick layers, but inspection of their dilute solutions or thin films shows that in even these the essential coloring matter is the same as in the other oils, but there is superimposed a small amount of material which has different color absorption and shows up quite differently in the thicker layers.

Further work is now under way to determine any special characteristics which may be associated with the color of crude oils from different sources.

Laboratory Directions

APPARATUS—The necessary apparatus is as follows:

1—Duboscq colorimeter with two 50-mm. cups and one 100-mm. cup (with glass cover).

2—Three film spacers as follows (see Note 1 for calibration):

No. 1 = 1.10 mm. thick ± 5 per cent
No. 2 = 0.380 mm. thick ± 5 per cent
No. 3 = 0.140 mm. thick ± 5 per cent

3—A standard solution of oil for comparison, of about 35° Lovibond color (see Note 2 for calibration).

METHOD OF PROCEDURE—Let the standard be designated by L. S. and the unknown oil by X. The division of the oils into the following classes is made in order to require a depth of standard of 4 to 12 mm.

Oils of True Color Range from 9 to 120—Obtain a uniform sample of X and pour it into the Duboscq cup, placing the cup on the right hand side of the instrument, L. S. being in the left hand cup. Use the regular 50-mm. cup for oils of a true color between 3 and 120, and the 100-mm. cup for oils lighter than 3 (Note 3). Adjust the plunger quickly on the nearest mm. reading in X so as to obtain a 5 to 20 mm. reading of L. S. Then move the L. S. plunger carefully until a color match is obtained, approaching a match from both the light and dark side (Note 4). One reading is sufficient, but three may be very quickly made and a check thereby obtained. Record as data the reading in mm., *a*, of L. S. necessary to match a definite layer, *b* mm., of oil X.

Oils of True Color Range from 120 to 4500—Stir X carefully to obtain uniformity and deliver a sample of several drops on the middle of the glass film plate which has the suitable spacers, as indicated in Plate IV. The film plates must be very clean and free from dust particles. Press down the top plate over the sample, squeezing out any excess of oil through the sides, and clamp the plates with suitable fasteners (Note 5). Clean the top and bottom surfaces and insert the film of oil beneath the plunger on the right hand side of the colorimeter, lowering the plunger until it rests lightly on the surface of the top plate, entirely covering the oil film. Move the L. S. plunger to obtain a match as before and record as data the reading in mm., *a*, of L. S. necessary to match the layer *b* (the thickness of film used) of X.

CALCULATION OF TRUE COLOR VALUE—

At match: a mm. = reading of L. S. for reading of b mm. of X oil.
For 1 to 120 T. C. range, b = layer of X oil in cup.
For 120 to 4500 T. C. range, b = thickness of oil film in spacers.

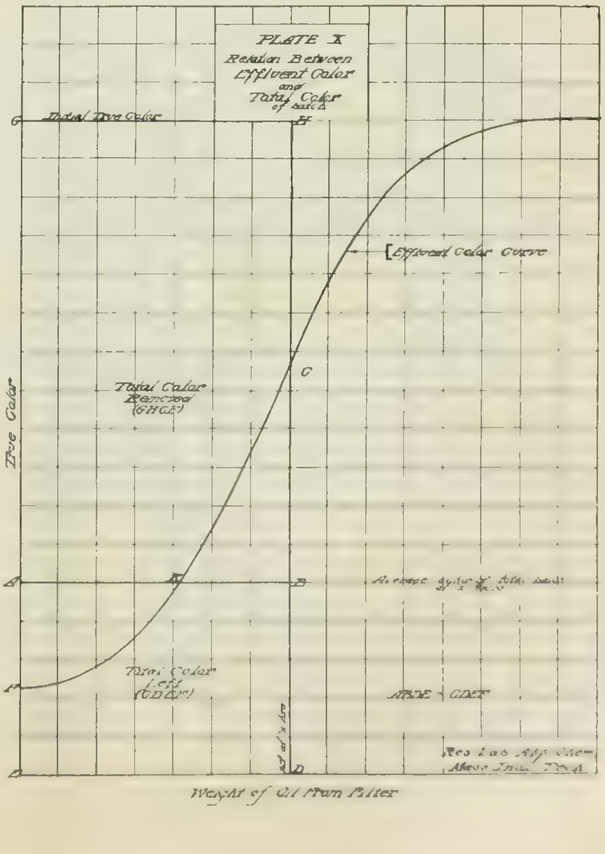
Then let C_x = unknown color, and 35 = color of L. S.

$$\text{and } \frac{C_x}{35} = \frac{a}{b} \text{ or } C_x = \frac{a}{b}(35).$$

If a is chosen arbitrarily at 5 or 10 mm. then

$$C_x = \frac{175}{b} \text{ or } \frac{350}{b}, \text{ respectively.}$$

When the film spacers are used the true color may be obtained easily from Plate IV, which gives true color readings for L. S. readings matching the films. If desired, simple charts or tables may be prepared to record the true color



readings corresponding to different levels of the L. S. plunger and the different films used, thus simplifying the calculation for plant use.

Notes

1—Film spacers are selected as previously outlined, namely:

For oils of T. C. range from 120– 400 = No. 1
For oils of T. C. range from 400–1100 = No. 2
For oils of T. C. range from 1100–4500 = No. 3

The thickness is accurately determined by measuring with a micrometer to 0.0001 in., obtaining the thickness of each plate separately and then the over-all measurement. A proper selection of microscope slides is made and the spacers assembled according to Plate III. Film plates should be marked and always kept in pairs.

2—To prepare L. S. make up the following solutions:

Solution A—Unfiltered cylinder stock dissolved in water-white kerosene and approximately matching a 350 Lovibond oil.

Solution B—Filtered oil dissolved in kerosene to match approximately a 350 oil.

Mix approximately in the proportion A : B :: 20 : 80 by volume to obtain L. S. and in the reverse proportion to obtain the special dark standard D. S. Dilute L. S. and D. S. with kerosene until both give a reading of 9.1 mm. when matched against a 50° Lovibond color glass (oil series). This 50° Lovibond glass should be carefully checked against two 25° glasses or other combination to avert any error due to an irregularity in the 50° glass. If any difficulty is experienced in matching colors from 1500 to 4500 use the D. S. (dark standard). Other standards may be made if necessary for special work and the true color value obtained by comparison with L. S. or D. S. Both L. S. and D. S. are exactly equivalent in color value, D. S. merely possessing a slightly grayer tint than L. S. which makes it easier to get a good match in some cases. For experienced observers a single standard L. S. is sufficient to cover the whole range of color determinations.

3—For oils of T. C. between 3 and 200 the 50-mm. cup is used, the plunger being set at 5, 10, 20, or 40 mm., according to the unknown oil color. For oils lighter than 3, as previously stated, the plunger is unscrewed and the oil placed in a special cell 100 mm. deep, equipped with a glass cover which fits evenly on the top and squeezes out any excess oil.

4—It is more convenient to adjust L. S. rather than X, since in the very light oils the plunger is very near the surface of X and permits of only a slight variation in depth. With oils where the film spacers are used L. S. is always varied; for the sake of uniformity, this procedure is recommended throughout the whole range. Calculation may also be somewhat simplified as indicated above if definite thicknesses of the unknown are always used. If any bubbles adhere to the bottom of plunger they should be removed by tapping or by raising and lowering the plunger slightly, as these air bubbles cause errors in the color determination.

5—Any type of fastener exerting uniform pressure on the spacers may be used. Small sized paper clips are very satisfactory. Even very moderate pressure is sufficient to reduce the oil film on the spacers to an inappreciable thickness. A special type of metal holder for the film spacers has been devised which may be used with the colorimeter. By washing with gasoline the residual oil is very thoroughly and quickly removed.

Source of Light—Use ordinary daylight or the special daylight lamp. By using either the mirror or milked glass side of the Duboscq reflector at different angles the intensity of the light may be varied at will, without any effect on the color values obtained. There is, however, a certain range in amount of light which gives the best matches without eye strain, and care should be taken not to get too much or too little light.

Acknowledgment

The writers desire to express their appreciation for the hearty coöperation of the men on the laboratory and plant staff of the Vacuum Oil Company at Rochester, whose assistance and suggestions during the progress of this work have been invaluable.

Simple Hydrogen Generator for Use in Making Hydrogen-Ion Concentration Measurements

By Paul H. Cathcart[1]

Research Laboratories, National Canners' Association,
Washington, D. C.

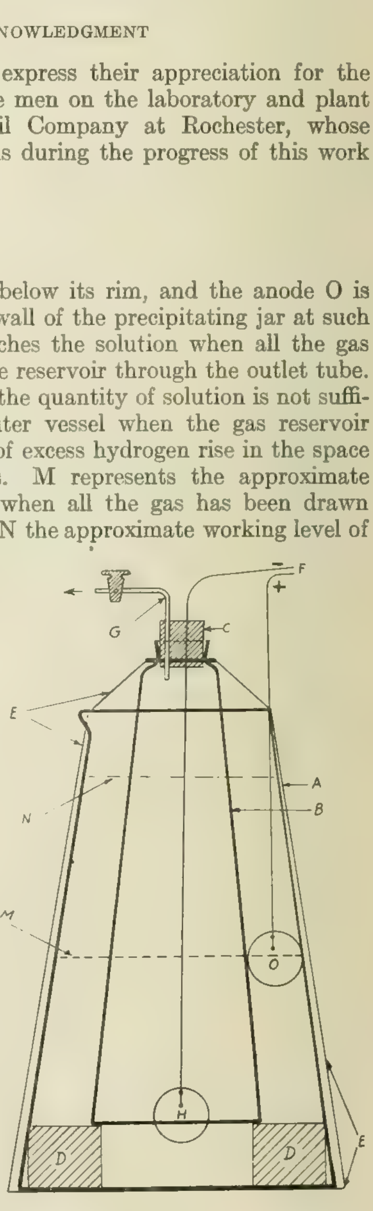
The principle involved is that of a bell jar inverted in a cylinder containing a 10 per cent sodium hydroxide solution. Two electrodes on a 110-volt D. C. circuit are introduced, the cathode within the bell jar and the anode outside and at a higher level. The outer vessel, A, consists of a large glass precipitating jar about 15 in. high, while the hydrogen reservoir is a large percolator, B, of about the same height, inverted and placed inside the precipitating jar and held about an inch from the bottom by means of glass or porcelain blocks or a porcelain acid dish, D.

This slight elevation is to allow the cathode H, which is on a wire introduced through the rubber stopper C sealed in the top of the percolator, to dip slightly below the rim of the reservoir. To keep the reservoir from rising when full of hydrogen it is held down by rubber covered wires, E, fastened around the neck and running at four places down the outside of the precipitating jar and under its bottom, where they are laced together in such a way that they cannot slip off.

A glass tube, G, with a stopcock passes through the rubber stopper at the top and leads the collected hydrogen through the purifying train to the hydrogen electrode cells. The electrodes and wires which are in contact with the caustic solution are of iron and have given perfect satisfaction. The electrodes, each of about 4 sq. in. area, were stamped out of ordinary tin plate and stripped of tin with a solution of sodium plumbate (lead acetate plus an excess of sodium hydroxide). The cathode H is adjusted within the reservoir so that it projects just below its rim, and the anode O is adjusted near the inside wall of the precipitating jar at such a height that it just reaches the solution when all the gas has been drawn out of the reservoir through the outlet tube. Care must be taken that the quantity of solution is not sufficient to overflow the outer vessel when the gas reservoir is full and large bubbles of excess hydrogen rise in the space between the two vessels. M represents the approximate level of NaOH solution when all the gas has been drawn out of the reservoir, and N the approximate working level of NaOH solution when the reservoir is full of gas.

The generator is kept in a sink as a matter of convenience in case of overflow or breakage. An ample supply of hydrogen has been maintained at all times by having a lamp bank drawing a current of about 4 amp. connected in series with the electrodes. Whenever the reservoir becomes full and overflows a switch in the circuit is opened and the generation of gas is stopped until again needed.

The lamps on the bank are arranged in parallel and fastened on a board which is inverted over a small sink so that about half of the bulbs are immersed in flowing water the height of which is regulated by an overflow tube. This gets rid of both the glaring light and the heat from the lamps.



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[1] Received December 1, 1921.

Changes in Some Varnish Resins on Heating[1]

By **F. H. Rhodes**[2] and **H. F. Johnson**

Department of Chemistry, Cornell University, Ithaca, New York

In varnish manufacture resins are rendered soluble in oil by a preliminary heating ("running") at 325° to 350° C. The present paper deals with the nature and extent of changes in the acid and iodine numbers of resins on heating. Determinations were made on Congo copal, East India copal, Manila copal, Pontianak, and kauri, on the original resins and on samples which had been heated to 300°, 350°, and 390° C.

In every instance heating caused a decrease in acid value, the extent varying with different resins. The iodine number of Congo copal decreased upon heating, and that of East India copal increased. For the other resins, the value increased slightly when they were heated to 300 C. but decreased at higher temperatures. There is no apparent relation between the change in iodine number, acid value, and loss in weight on heating.

As is well known, ordinary oleoresinous varnishes consist essentially of solutions of "varnish resins" in drying oils. Among the resins which are most commonly used in varnish-making are various natural resins of fossil or semifossil origin—Congo, East India, Manila, and Pontianak copals, and kauri. These resins are not, in general, directly and completely soluble in oil, but may be rendered soluble by heating to fusion and partial decomposition. In actual practice, this preliminary heating or "running" of the resin is effected by heating it to a temperature of approximately 325° to 350° C.

When the resin is thus heated a certain amount of decomposition takes place, volatile products are given off, and the residue becomes more soluble in oil or other solvents than was the original resin. Very little work has been done to determine the actual chemical changes which take place in the resins on heating, and little or nothing is known as to the exact nature of the chemical reactions which occur in "running" the varnish resins.

A number of investigators have determined the analytical constants of the various fossil and semifossil resins. Worstall[3] determined the acid numbers and the iodine values (Hubl) of a rather large number of samples of Manila, Pontianak, South African, West African, Sierra Leone and Brazilian copals, kauri, and dammar. He also showed that some of these fossil resins, when finely ground and exposed to air for 4 mo., showed an increase in the acid number and a decrease in iodine value. These changes he attributed to the oxidation of the resin.

Williams[4] determined the "KOH absorption" and the iodine value of a kauri and copal, both before and after "running." He examined, however, only one sample of each type of resin, and gives no information as to the type or source of the copal which he used. Moreover, he does not state the temperature to which the resin was heated during "running."

Lewkowitsch[5] determined the analytical constants of a number of varnish resins, both before heating and after heating to 300° C. The results obtained with the original resins differ markedly from Worstall's results for the same constants of similar types of resins. Moreover, in "running" his resins, Lewkowitsch heated the resins to a temperature of 300° C. only, whereas in the actual manufacture of varnishes the resins are usually heated to temperatures appreciably higher than this.

The work described in this present article was done for the purpose of determining the nature and extent of the changes in the acid numbers and the iodine numbers of the varnish resins when these resins are heated to various temperatures. It was hoped that the results thus obtained would afford some information as to the nature of the chemical changes which occur in the "running" of varnish resins.

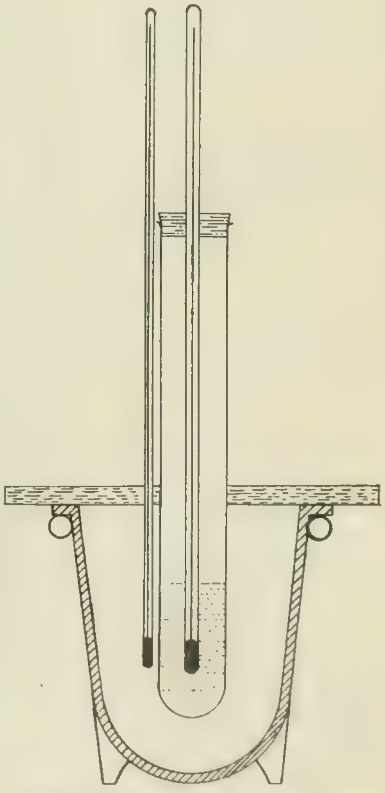
Materials and Method

The following resins were used:

Congo Copal, bold amber, donated by S. C. Johnson & Son Co.
Kauri, Grade No. 1, donated by S. C. Johnson & Son Co.
East India Copal, nubs, donated by S. C. Johnson & Son Co.
Pontianak Copal, selected fine, donated by A. Klipstein & Co.
Manila Copal, bright amber, from Patterson, Boardman, Knapp Co.

In all cases, the iodine numbers of the resins were determined by the Hubl method, following the exact procedure described in Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats and Waxes."[6] The acid numbers were determined by the indirect method used and described by Worstall.[3] To 1 g. of the finely powdered resin weighed out in a glass-stoppered bottle, 15 cc. of benzene, 5 cc. of alcohol, and 15 cc. of 0.2 *N* alcoholic potash solution were added. After 18 hrs., 25 cc. of alcohol and a few drops of phenolphthalein were added and the excess of alkali was titrated with 0.2 *N* sulfuric acid. The number of milligrams of potassium hydroxide neutralized by the gram of resin was taken as the acid value of the resin.

This method would, of course, give incorrect results if the resins contained esters as well as free acid or acid anhydrides, but Worstall has shown that esters are not normally present in these fossil or semifossil resins.



Apparatus Used for "Running" Resins

When the original Manila and Pontianak copals were analyzed by this method, the resins dissolved completely in the mixed solvent. The original East India and Congo copals and kauri resin, however, did not dissolve completely even on long standing, and therefore the acid values obtained for these results are possibly lower than the true

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[1] Received December 22, 1921.

[2] Professor of Industrial Chemistry.

[3] *J. Am. Chem. Soc.*, **25** (1903), 860.

[4] *Analyst*, **23** (1898), 254.

[5] *Ibid.*, **26** (1901), 37.

[6] 5th edition, 1, 395.

acid values. All of the resins which had been heated to fusion dissolved readily and completely in the mixture of alcohol and benzene, and gave results which are presumably correct.

Apparatus

The apparatus used in these experiments is shown in the accompanying figure. The resin was contained in a large test tube (1 in. × 8 in.). This tube extended, through a piece of asbestos board, into a hemispherical iron pot which was heated by a Méker burner and served as an air bath to secure uniform heating of the resin in the tube. An accurate thermometer was used to indicate the temperature of the resin in the tube, while a second thermometer placed beside the tube served to indicate the temperature of the air bath.

A weighed amount (usually about 10 g.) of the resin was heated in the apparatus until melted. The heating was then continued at the rate of 3° C. per min. until the desired final temperature was attained. The resin was kept at the final temperature for 5 min. The melted resin was stirred from time to time to insure uniform heating. Tube and resin were removed from the air bath and cooled rapidly by holding in a blast of air and finally by immersing in cold water. The final product was weighed and analyzed.

Results

The results obtained in these experiments are shown by Tables I, II, and III.

Table I—Change in Acid Numbers

	Original	Acid Value after Heating to 300° C.	350° C.	390° C.
Congo copal	176	136	104	98
Kauri	129	100	90	72
East Indian copal	56	45	36	24
Manila copal	169	156	137	132
Pontianak	176	132	115	101

Table II—Change in Iodine Values

	Original	Iodine Number (Hubl) after Heating to 300° C.	350° C.	390° C.
Congo copal	126	109	97	96
Kauri	112	115	104	104
East Indian copal	75	78	90	100
Manila copal	117	122	122	116
Pontianak copal	120	124	122	96

Table III—Loss in Weight

	Percentage Loss after Heating to 300° C.	350° C.	390° C.
Congo copal	3.8	9.5	48.6
Kauri	22.2	22.4	28.4
East Indian copal	6.05	8.5	22.6
Manila copal	4.9	10.6	22.5
Pontianak copal	7.6	9.3	23.0

It will be observed that in every case the heating of the resin results in a marked decrease in the acid value. This is presumably due to the splitting off of carboxyl groups and the evolution of water and carbon dioxide. This hypothesis is supported by the observation that water and carbon dioxide are evolved during the "running" of varnish resins. With Congo and Manila copals the decrease in acid value is substantially complete at 350° C., while kauri and Pontianak copal show further marked decrease in acid value with increased temperatures of heating.

The different resins gave markedly different results for the change in iodine value on heating. With Pontianak and Manila copals the iodine value increased somewhat at 300° C., showed little further change at 350° C., and decreased again at 390° C. Kauri, after heating to 300° C., showed an increased iodine value, but further heating resulted in a decrease to below that of the original resin. The iodine value of Congo copal decreased as the temperature increased, while that of East India copal increased progressively with the temperature.

These changes may be assumed to be due to several different types of reaction which may occur simultaneously in the heated resins. Either polymerization or absorption of oxygen at the unsaturated groups would decrease the iodine number; while cracking or depolymerization would increase the absorption of iodine. Worstall has shown that when finely powdered copals are allowed to stand in the air, oxygen is absorbed and the iodine values decrease. This absorption would presumably take place more rapidly at elevated temperatures, and would account partly for some of the observed changes. On the other hand, the volatile products formed during the "running" of varnish resins contain relatively large amounts of hydrocarbons which are obviously produced by the cracking or partial depolymerization of the resin substance.

Apparently the direction and the extent of the change in iodine value are determined by the relative extent to which these various reactions—oxidation, polymerization, cracking, and depolymerization—occur in the heated resin; this, in turn, will depend on the nature of the resin and upon the temperature to which it has been heated.

There is no apparent relation between the loss in weight on heating and the change in iodine number or the change in acid value.

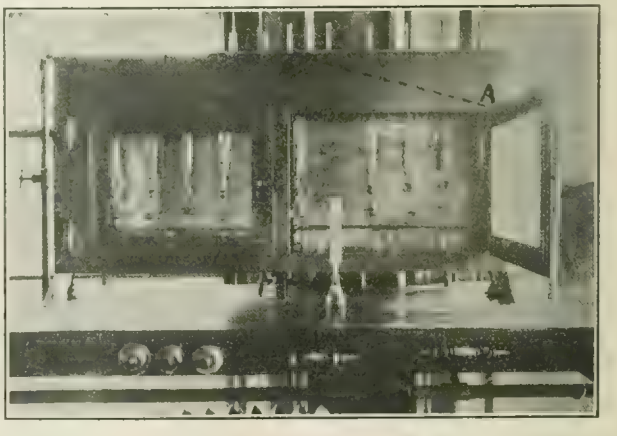
Fat Extraction Set[1]

By R. D. Scott

State Department of Health, Columbus, Ohio

The fat extraction set described has proved very satisfactory for stock feed and other routine analyses. The cabinet and condensing tank were made up by a local tinsmith from 16-oz. tinned copper. The cabinet is 48 × 18 × 4.5 in., and the condensing tank, 47.5 × 4 × 4 in. The twelve condenser tubes are of $^3/_8$-in. block tin, each 30 in. long, and lie in the position A–A.

Heat is provided not by hot plates, but by "space heaters," heating strips obtainable at electrical supply houses at about one-tenth of the cost of an electric hot plate. The two used are rated at 125 volts, 4 amperes, and when connected in series give the proper heat to boil ether, the bottom of the flasks being 2 in. above the heaters.



The flasks, thimbles, and outer glass tubes form the conventional Vivian type fat extractor, but porous clay thimbles are used instead of glass tube thimbles covered at the bottom with a filter paper supported by muslin.

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[1] Received December 9, 1921.

Recrystallization of Niter Cake at 12°[1]

By **Blair Saxton**[2]

Department of Chemistry, Yale University, New Haven, Conn.

In the following paper equations and curves have been developed by means of which the crystallization at 12° of the various solid phases of the system Na_2SO_4–H_2SO_4–H_2O can be followed.

Calculations have been made showing the extent of separation into solution and solid, especially as $Na_2SO_4.10H_2O$, which can be effected at 12°.

In a previous article,[3] the possibility was considered of separating niter cake into its components by recrystallization at 25°. Since that time, solubility results have been obtained by Foote[4] at 12° for the system Na_2SO_4–H_2SO_4–H_2O, so that the possible separations at the latter temperature can now be determined. This system has also been studied recently by Pascal and Ero[5] and by Dawson[6] at a number of temperatures. Dawson has also given results showing the amounts of Glauber's salt which can be crystallized at various temperatures.

The results, as given by Foote, expressed in per cent by weight, are given in Table I.

TABLE I

	Solution		
Solid Phases	H_2SO_4	Na_2SO_4	H_2O[1]
$Na_2SO_4.10H_2O$	0.00	9.49	90.51
	6.47	12.87	80.66
	12.90	18.02	69.08
$Na_2SO_4.10H_2O \rightleftarrows Na_2SO_4.NaHSO_4$	16.52	32.93	50.55
$Na_2SO_4.NaHSO_4$	21.95	29.59	48.46
$Na_2SO_4.NaHSO_4 \rightleftarrows NaHSO_4.H_2O$	27.96	25.42	46.62
$NaHSO_4.H_2O$	33.89	15.15	50.96
	36.69	11.82	51.49
	58.79	4.33	36.88
Composition of Salts			
$Na_2SO_4.10H_2O$	0.00	44.10	55.90
$Na_2SO_4.NaHSO_4$	18.70	81.30	0.00
$NaHSO_4.H_2O$	35.50	51.46	13.04

[1] By difference.

The results are plotted in Fig. 1, with per cents of acid in solution as abscissae, and per cents of sodium sulfate as ordinates. A diagonal is drawn across the diagram. This diagonal is then the hypothenuse of a right-angled triangle, each leg of which represents 70 per cent of acid and sodium sulfate, respectively. The per cent of water in solution is then represented by either the vertical or the horizontal distance of any point from the hypothenuse plus 30. The lines radiating from the origin represent the compositions of niter cakes of 20, 25, 30, and 35 per cent acid, together with a line for $Na_2SO_4.NaHSO_4$ and a line tangent to the curve AB. This latter line, as will be explained later, gives a graphical method of determining from what concentration of solution the maximum amount of Glauber's salt will crystallize at 12°. The intersection of any of the other lines from the origin with the solubility curve gives the composition of solution which first becomes saturated with the solid represented by that branch of the solubility curve intersected.

Starting from the solubility of pure Glauber's salt there are two univariant points, at each of which two solids are in equilibrium. The curves correspond to divariant systems with one solid phase in each. The phase Na_2SO_4 which is present at 25° drops out at 12°. The branches of the curve are not straight lines, except in the case of BC. In our former paper,[3] because of lack of data, the lines were assumed to be straight between the univariant points. Previous calculations of this kind have, in general, been made on similar assumptions. Dawson[6] has used the actual curves. He has recognized that at a certain acidity, which he has called "the optimum acidity," a maximum yield of Glauber's salt is obtained. Our identical conclusion (see below) was reached entirely independently. When the actual curves are considered some interesting results at once appear, especially in the case of the branch of the curve representing the solubility of Glauber's salt.

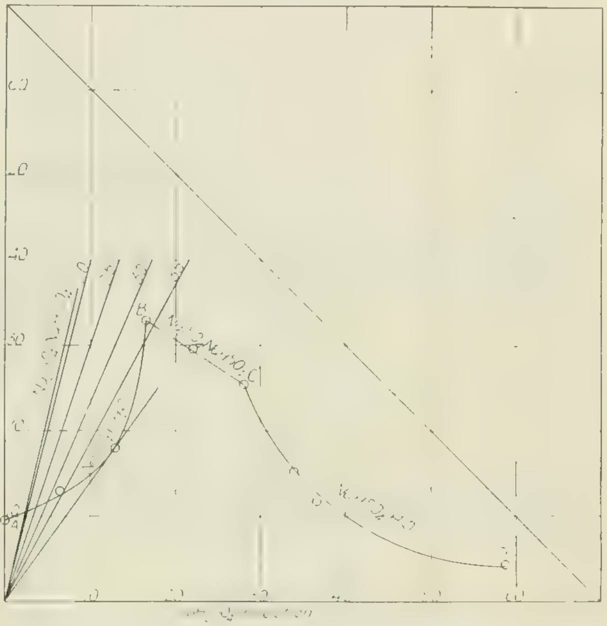

FIG. 1

THE CRYSTALLIZATION OF $Na_2SO_4.10H_2O$

The solubility of this solid is represented by the curve AB in Fig. 1. If we designate the concentrations of sodium sulfate and sulfuric acid in a water solution saturated with Glauber's salt by x and y, respectively, we obtain the following empirical equation for the curve:[7]

$$x = 5.58 + \frac{86.6}{19.69 - y}$$

The average deviation of values of x calculated by means of this equation from the values determined is ±0.40. If we represent the weights of Na_2SO_4 and H_2SO_4 in solution before crystallization by n and s and the weight of $Na_2SO_4.10H_2O$ separating from solution by z, then at any point along AB the following relation must exist:

$$\frac{n - 0.4410z}{s} = \frac{x}{y} = \frac{5.58 + \dfrac{86.6}{19.69 - y}}{y}$$

and, solving for z,

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[1] Received August 8, 1921.

[2] Assistant Professor of Chemistry.

[3] THIS JOURNAL, **10** (1918), 897.

[4] *Ibid.*, **11** (1919), 629.

[5] *Bull. soc. chim.*, **25** (1919), 35.

[6] Brit. Patent 127,677 (1919); *C. A.*, **13** (1919), 2421.

[7] The curve is very nearly a section of an equilateral hyperbola, the equation of which can be written $x = a + \frac{b}{c - y}$. The values of a, b, and c were evaluated by the method of least squares. The equation so derived represents the experimental facts better than any other simple equation, whether quadratic, logarithmic or exponential, which the author has tried.

$$z = 2.268\left(n - \frac{sx}{y}\right) = 2.268\left[n - \frac{s}{y}\left(5.58 + \frac{86.6}{19.69-y}\right)\right].$$

Examination of this equation shows that as $\frac{x}{y}$ decreases, the value of z increases for fixed values of n and s. In other words, the amount of $Na_2SO_4.10H_2O$ separating reaches a maximum when the concentration of Na_2SO_4 divided by the concentration of H_2SO_4 in the saturated solution is a minimum. This condition is represented graphically as the point at which a line from the origin becomes tangent to AB. The slope of this line is $\frac{x}{y}$ and no other line from the origin can intersect or touch AB and have a lesser slope. This point of maximum crystallization may be calculated by solving

$$\frac{x}{y} = \frac{5.58 + \dfrac{86.6}{19.69-y}}{y}$$

for minimum value of $\frac{x}{y}$, or the equation

$$z = 2.268\left[n - \frac{s}{y}\left(5.58 + \frac{86.6}{19.69-y}\right)\right]$$

for maximum value of z. Either of these methods gives $y = 11.83$, which is checked by the graphical method. This value of y is independent of the values of n and s; hence it is the same for any niter cake. Obviously it is the point on AB at which to stop crystallization. If we substitute this value of y in the general equation for z, we obtain

$$z = 2.268n - 3.181s,$$

or, for 100 parts of niter cake,

$$z = 226.8 - 5.449s.$$

In this case s represents the per cent of acid in the niter cake.

The weight, w, of water in the solution at crystallization is obviously given by the equation

$$\frac{w}{s} = \frac{100-(x+y)}{y}.$$

Substituting the value of x, in the terms of y, this becomes

$$w = \left(\frac{1773-94.4y}{(19.69-y)y} - 1\right)s.$$

For the maximum value of z, when y is 11.83, we find

$$w = 6.052s.$$

The weight, w', of water with which the niter cake must be leached is

$$w' = w + 0.559z = 1.268n + 4.274s.$$

The total weight, W, at crystallization is

$$W = w + 0.559z + n + s = 2.268n + 5.274s.$$

For 100 parts of niter cake

$$w' = 126.8 + 3.006s \text{ and } W = 226.8 + 3.006s.$$

The maximum point may better be recognized by the titer of the solution, which should show 11.83 per cent acid, or by its density. In speaking of crystallizing Glauber's salt we refer to crystallizing the hydrate to this maximum point.

A niter cake containing more than 41.6 per cent of acid will not deposit Glauber's salt from solution at 12°, but rather the double salt $Na_2SO_4.NaHSO_4$. This can be calculated from the values of x and y at the point of maximum crystallization. The percentage acidity of the solute is obviously $\frac{100\,y}{x+y}$. Since y at this point is 11.83, x, calculated from the equation of the line AB, becomes 16.60. These values of x and y give 41.6 as the per cent of acid in the solute or dissolved niter cake.

THE CRYSTALLIZATION OF $Na_2SO_4.NaHSO_4$

The solubility of this phase is represented by the line BC, the equation of which is

$$x = 43.79 - 0.6576y.$$

Starting with this and the equation

$$\frac{n-0.8130z}{s-0.1870z} = \frac{x}{y},$$

equations similar to those given for $Na_2SO_4.10H_2O$ can be developed. For any point on the line BC and for any weight of niter cake we have:

$$z = \frac{(43.79-0.6576y)s - ny}{8.19-0.936y}$$

$$w = (s-0.1870z)\left(\frac{56.21}{y} - 0.3424\right)$$

The maximum value of z is reached at C, for here $\frac{x}{y}$ is at its lowest value. That z increases as $\frac{x}{y}$ decreases can be seen by solving the original equation for z and arranging in the following form:

$$z = 5.35s + \frac{4.35s-n}{0.187\frac{x}{y} - 0.813}$$

For all niter cakes which will saturate water solution directly with $Na_2SO_4.NaHSO_4$, the numerator of this fraction is positive, while at any point on the line BC the denomination is negative. The fraction, therefore, becomes smaller and z becomes larger as $\frac{x}{y}$ decreases. At the point C, at which $y = 27.96$,

$$z = 1.555n - 1.414s$$
$$w = 2.110s - 0.4852n.$$

Or, if 100 parts of niter cake are considered,

$$z = 155.5 - 2.969s$$
$$w = w' = 2.595s - 48.51$$
$$W = w + 100 = 2.595s + 51.49.$$

At this point, C, the solution should show 27.96 per cent of acid. This is the point to which we have calculated all crystallizations[3] of this double salt.

Only a niter cake containing at least 33.4 per cent of acid can directly saturate water at 12° with this double salt. This can be calculated from the values of x and y for point B in Fig. 1. If the water solution of a niter cake containing less than this per cent of acid were crystallized at 12° so that the solution would contain more than 16.52 per cent of acid, corresponding to point B in Fig. 1, Glauber's salt would first crystallize until point B had been reached, then the double salt would separate. If equilibrium were reached, the solid phase would be double salt only until the concentration had been carried so far that the acidity of the solution in equilibrium with the solid had reached that corresponding to point C in Fig. 1, namely, 27.96 per cent.

THE CRYSTALLIZATION OF $NaHSO_4.H_2O$

The solubility of this phase is represented by the curve CD, which, as far as it has been carried, follows the equation

$$x = 35.15 - \sqrt{y(115.5-y) - 2360}.$$

This is the equation for a circle the center of which is only slightly to the right of D and a little above C in Fig. 1. For points beyond D the equation is useless, but for the curve as determined it serves very well. The point D, furthermore, cannot be far from the univariant point at which $NaHSO_4$ and its monohydrate coexist, so in considering CD as a regular curve we cannot be far wrong. From this equation and the relation

$$\frac{n-0.5146z}{s-0.3550z}=\frac{x}{y}.$$

Values for z and w as follows are obtained

$$z=\frac{s\left[35.15-\sqrt{y(115.5-y)-2360}\right]-ny}{0.3550\left[35.15-\sqrt{y(115.5-y)-2360}\right]-0.5146y}$$

$$w=(s-0.3550z)\left(\frac{64.85+\sqrt{y(115.5-y)-2360}}{y}-1\right)$$

These calculations are not so laborious as they appear, since the value of the radical is easily simplified for a given value of y.

This solid phase contains 35.50 per cent of acid and only a niter cake containing at least 52.4 per cent of acid can directly saturate water with this solid at 12°.

If, however, $Na_2SO_4.NaHSO_4$ has been crystallized from the solution of a cake which originally contained less than 52.4 per cent of acid, and the per cent of acid in the solute has thereby been increased, $NaHSO_4.H_2O$ may be separated from solution. Any desired acid concentration along CD may then be reached.

PROCESSES

PROCESS A—Remove $Na_2SO_4.10H_2O$ from solution by using the proper amount of water to reach but not exceed the point of maximum yield; or completely leach with the correct amount of water. A method of calculating this amount has been given. The solid if properly washed will be fairly pure Glauber's salt. Per 100 parts of niter cake the maximum amount, z, of Glauber's salt which can be obtained in this way is $(226.8-5.449s)$. This expression is linear with respect to s; in Fig. 2 z has been plotted against s. From this plot one can read at once the maximum yield of the decahydrate obtainable from 100 parts of a cake which is s per cent acid. The weight of water, w', with which the cake should be leached is also a linear function of s, as can be seen from Fig. 3. No advantage would be gained by adding fresh niter cake and water to the residual solution from this process. One would accomplish nothing except the adding of the solution residues as each crystallization or leaching is carried out.

PROCESS C[8]—Remove $Na_2SO_4.NaHSO_4$ from solution by concentrating to the point C in Fig. 1. The solution will contain 28.0 per cent of acid. The water required for complete leaching has been discussed. The solid has 18.7 per cent of acid, and, unlike Glauber's salt, has little apparent value. It is simply an added batch of 18.7 per cent niter cake. There are two reasons, however, for its removal from solution. First, it permits concentration of acid in the residual solution up to 28 per cent. Second, it may be put through Process A either alone or with a new lot of niter cake and more Glauber's salt removed. Both z and w' are linear functions of s, and are plotted in Figs. 2 and 3. The equations relating to these values have been given.

PROCESS AC—Process C may follow A; that is, $Na_2SO_4.10H_2O$ may be first removed and then $Na_2SO_4.NaHSO_4$ may be separated from the filtrate. One hundred grams of solute, after Glauber's salt has been removed from the solution of any niter cake, will contain 58.37 g. of Na_2SO_4 and 41.63 g. of H_2SO_4. On concentrating to 160 g. or to the appropriate titer, 31.9 g. of $Na_2SO_4.NaHSO_4$, composed of 25.9 g. of Na_2SO_4 and 6.0 g. of acid, will separate. Or, if we consider 100 parts of the original cake, containing s parts of acid, the weight of $Na_2SO_4.NaHSO_4$ which will separate after Glauber's salt has been removed is $0.767s$. This linear relation between the amount of acid sulfate and the acid in the original cake is plotted in Fig. 2. The amount of water in solution after the acid sulfate has been removed is also a linear function of s and is plotted in Fig. 3.

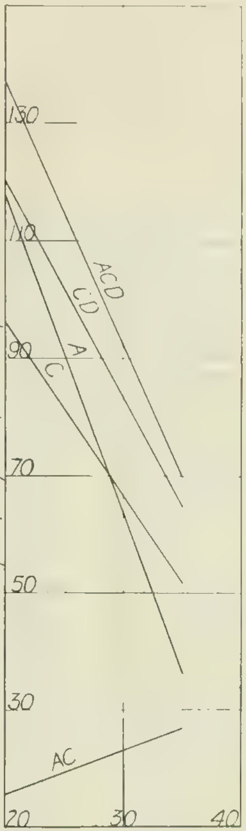

FIG. 2

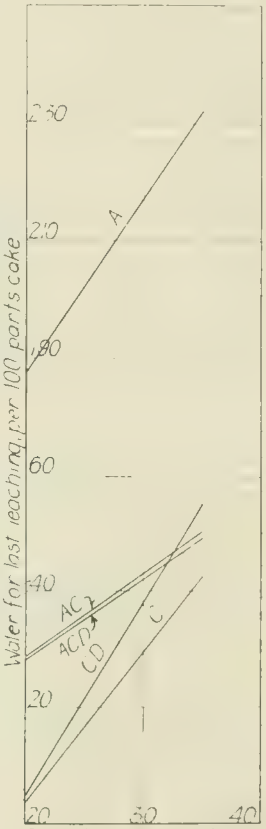

FIG. 3

PROCESS D—Recrystallize the $Na_2SO_4.NaHSO_4$ from C. If Glauber's salt only is desired, the above acid sulfate can be put through Process A. One hundred grams of $Na_2SO_4.NaHSO_4$ so treated will give 124.9 g. of the decahydrate, of which 55.1 g. are Na_2SO_4, by evaporating to 283.0 g., or by leaching with 183.0 g. of water. The titer of the solution by which this operation may be followed has been given. In this way 67.8 per cent of the Na_2SO_4 in the acid sulfate may be recovered as Glauber's salt.

PROCESS D'—If it is desired to concentrate the solution in sulfuric acid, $Na_2SO_4.NaHSO_4$ may be crystallized from the solution from D by using Process C. The weight of solute after 124.9 g. of Glauber's salt have been removed is 44.92 g., of which 26.22 g. are sodium sulfate and 18.70 g. are sulfuric acid. From the solution 14.33 g. of $Na_2SO_4.NaHSO_4$, containing 11.65 g. of Na_2SO_4 and 2.68 g. of H_2SO_4, can be removed. By these two operations 82.1 per cent of the sodium sulfate in the original acid sulfate as $Na_2SO_4.NaHSO_4$, 67.8 per cent as Na_2SO_4, and 14.3 per cent as $Na_2SO_4.NaHSO_4$, will have been removed from solution and 85.7 per cent of the acid will be left in solution. Naturally this cycle could be repeated as many times as desired, each time recrystallizing the $Na_2SO_4.NaHSO_4$. In this way practically all of the acid sulfate could be worked into Glauber's salt, but the number of operations necessary makes such a cycle seem impracticable. However, these operations could be run continuously, new niter cake being added and the sodium nearly entirely separated as Glauber's salt.

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[8] Process B was used in our previous paper to designate the separation of Na_2SO_4 which is here absent.

PROCESS ACD—Glauber's salt has been removed from solution, then $Na_2SO_4.NaHSO_4$, and this has been recrystallized by Method D. This combined process gives nothing but decahydrate, but leaves two solutions, one after C, containing 28 per cent of acid, the other after D, containing only 11.8 per cent of acid. Again considering 100 parts of niter cake, the total amount of decahydrate obtained by this method is $226.8-4.491s$ and hence is a linear function of s. This and the water in the solution after the last step are plotted in Figs. 2 and 3.

PROCESS CD—$Na_2SO_4.NaHSO_4$ has been crystallized from the solution of the original niter cake and then the acid sulfate has been recrystallized by Process D. The amount of Glauber's salt obtainable in this way from 100 parts of niter cake containing s per cent of acid is given by the equation $z = 194.2-3.708s$. This and the quantity of water necessary for the recrystallization is a linear function of s. The lines showing these relations are in Figs. 2 and 3, respectively.

PROCESS ACD′—If this process were used, from 100 parts of niter cake which was s per cent acid, the total amount of Glauber's salt obtained would be $226.8-4.491s$ and the $Na_2SO_4.NaHSO_4$ crystallized would be $0.1099s$.

PROCESS E—Remove $NaHSO_4.H_2O$ from solution. As has been stated, this cannot be done directly except in the case of a niter cake or solute high in acid. This process may, however, follow C, although the number of operations is such that it is practically excluded. If a solution high in acid were desired even at the expense of a complicated process and the loss of some acid in the solute, E might be resorted to. Solutions from 28 per cent to at least 59 per cent acid could be obtained. One hundred grams of solute from C will contain 47.6 g. of Na_2SO_4 and 52.4 g. of H_2SO_4. The results which can be obtained from such a solute can be calculated by means of the general equation for this acid sulfate.

RESULTS

The results which can be obtained by the use of these various processes are given in Table II and plotted in Fig. 2.

TABLE II

H_2SO_4 in Niter Cake Per cent	Treatment	No of Operations	Wt. of Water to Leach	Wt. of Solid. $a = Na_2SO_4.10H_2O$. $c = Na_2SO_4.NaHSO_4$	Acidity of Solution Per cent	H_2SO_4 Recovered in Solution Per cent	Na_2SO_4 Removed as Solid Per cent
20	A	1	187.0	$a=117.8$	11.8	100.0	64.9
	C	1	3.4	$c=96.1$	28.0	10.2	97.7
	AC	2	28.6	$a=117.8$; $c=15.3$	28.0	85.7	80.5
	ACD	3	28.0	$a=137.0$	28.0;11.8	100.0	75.5
	CD	2	4.4	$a=120.0$	28.0;11.8	100.0	66.2
25	A	1	202.0	$a=90.6$	11.8	100.0	53.3
	C	1	16.4	$c=81.3$	28.0	39.2	88.1
	AC	2	35.8	$a=90.6$; $c=19.2$	28.0	85.7	74.0
	ACD	3	35.1	$a=114.5$	28.0;11.8	100.0	67.3
	CD	2	21.2	$a=101.5$	28.0;11.8	100.0	59.7
30	A	1	217.0	$a=63.3$	11.8	100.0	39.9
	C	1	29.3	$c=66.4$	28.0	58.6	77.1
	AC	2	42.9	$a=63.3$; $c=23.0$	28.0	85.7	66.6
	ACD	3	42.1	$a=92.1$	28.0;11.8	100.0	58.0
	CD	2	38.0	$a=83.0$	28.0;11.8	100.0	52.2
35	A	1	232.0	$a=36.1$	11.8	100.0	24.4
	C	1	42.3	$c=51.6$	28.0	72.4	64.5
	AC	2	50.0	$a=36.1$; $c=26.8$	28.0	85.7	58.0
	ACD	3	49.1	$a=69.6$	28.0;11.8	100.0	47.1
	CD	2	54.8	$a=64.4$	28.0;11.8	100.0	43.7

An examination of Table II and Fig. 2 shows that for the Processes A, C, ACD, and CD the yield of crystals decreases as the per cent of acid in the niter cake increases. Only in one case, that of AC, is the reverse true for one of the solids, $Na_2SO_4.NaHSO_4$. Since Process A has preceded C in this combined process and the yield of Glauber's salt decreases in A much faster than that of the acid sulfate increases in C, the result is that the total weight of sodium sulfate, calculated as Na_2SO_4, falls off as the per cent of acid in the original niter cake increases.

A comparison of the methods for producing $Na_2SO_4.10H_2O$ shows that, of those here outlined, ACD is the most effective for a niter cake of less than 41.6 per cent acid, while CD, involving one less operation, is most effective when the original cake has more than that amount of acid. The difference in the yield of Glauber's salt is probably not great enough to warrant the extra operation required by Process ACD even with niter cakes low in acid. The other method, A, is the simplest. The yield of Glauber's salt, however, is the poorest. If the niter cake is comparatively low in acid, say, between 20 and 30 per cent, this process compares quite favorably with CD and is less expensive. We would recommend it for such niter cakes. The relations between the yields obtained by these three processes can be seen by a study of Table II, or by a glance at Fig. 2.

If it is desired to crystallize $Na_2SO_4.NaHSO_4$, the amount which can be separated can be found in the table or read from the figure.

In order to test these calculations, crystallization experiments were carried out with synthetic 30 per cent niter cake so that in the one case Glauber's salt was separated near the point of maximum yield, and in the other case $Na_2SO_4.NaHSO_4$ was crystallized.

In the first experiment 70.03 g. of anhydrous sodium sulfate were treated with 31.35 g. of 95.6 per cent pure acid. The cake, therefore, weighed 100.00 g. and contained 29.97 per cent of acid. To this were added 217.74 g. of water which, with that in the acid, made the total water 219.12 g. On warming slightly all sodium sulfate dissolved and Glauber's salt only crystallized at 12° after the solution was inoculated. This solution, in a stoppered Erlenmeyer flask, was left in a thermostat at 12° for 4 days during which it was frequently shaken. At the end of that time the Glauber's salt was filtered through a suction filter and quickly pressed between filter paper until it was dry. The yield was 60.2 g. The solution, on analysis, proved to contain 11.62 per cent of acid. The yield of Glauber's salt calculated is 63.4 g. The agreement is satisfactory, considering the roughness of the experiment.

In the second experiment 100.34 g. of synthetic niter cake, containing 30.01 per cent of acid, were dissolved in 56.73 g. of water. After warming until the sodium sulfate had dissolved, the solution was treated as in the previous experiment. The crystals were quickly filtered, washed twice with small portion of D'Ans' solution (5 volumes of water, 1 volume of concentrated sulfuric acid, and 7.5 volumes of ethyl alcohol), then with a little absolute alcohol, and finally with ether. After being air-dried, it weighed 40.4 g. Its analysis gave 18.56 per cent of acid, while the calculated per cent for $Na_2SO_4.NaHSO_4$ is 18.70. From the total weight at crystallization and equations previously given the calculated per cent of acid in the solution was 19.32. That found was 19.44. For this acidity and for the weight of niter cake taken the estimated yield of acid salt is 43.2 g., which is in satisfactory agreement with the weight found.

Butler and Dunnicliff[9] have apparently questioned the conclusion in the previous paper[3] that we obtained $Na_2SO_4.NaHSO_4$ in confirmation of calculations there developed. Their criticism is directed at the method of washing the acid sulfate as recommended by D'Ans. This consists in washing first with a mixture of alcohol and dilute sulfuric acid, then with alcohol, and finally with ether. They have shown that an acid sulfate such as $NaHSO_4.H_2O$ on prolonged extraction with moist ethyl alcohol will lose water and acid,

[9] *J. Chem. Soc.*, **117** (1920), 649.

forming $Na_2SO_4.NaHSO_4$ and finally Na_2SO_4. We do not question this conclusion. We do maintain, however, that their implication that we might not have had $Na_2SO_4.NaHSO_4$ but a salt higher in acid which several washings with 95 per cent alcohol had changed into this double salt is not justified. It is rather improbable that one could transform 108.2 g. of $NaHSO_4.H_2O$ into 68.5 g. of $Na_2SO_4.NaHSO_4$ by a few washings of well-defined large crystals with 95 per cent alcohol. Further, 108.2 g. of the monohydrate, which is the amount required to give 68.5 g. of the double salt, contain 38.4 g. of acid, which is more than the amount present in the solution from which the crystals separated. We claim our calculations have been confirmed. Further, the fact that not only the yield of $Na_2SO_4.NaHSO_4$, but that of Na_2SO_4, which, aside from its small solubility, is not affected by D'Ans' solution, corresponds to the calculated value argues in favor of our conclusion.

The criticism cited would also refer to the solubility determinations of Foote[4] on which the present calculations are based. Foote, however, had no difficulty in identifying the acid sulfates $Na_2SO_4.NaHSO_4$ and $NaHSO_4.H_2O$ even though he used D'Ans' solution for removing mother liquor.

The experiment on crystallizing $Na_2SO_4.NaHSO_4$ cited in the present paper would likewise be open to their criticism. Yet the double salt obtained is homogeneous and forms in well-defined crystals. Four different 5-g. samples gave 18.55, 18.55, 18.56, and 18.58 per cent of acid, which is rather better than one would expect from crystals of a higher acid salt which had been altered on the surface during the process of washing.

In conclusion, we wish to emphasize a statement in a previous paper[3] that our results and those of others[10] point to the conclusion that the separation of Glauber's salt is the better the lower the temperature. The lower temperature limit is the cryohydric temperature for the particular niter cake in question. This fact has been used to advantage in several patented processes. E. Hart[11] obtains granular sodium sulfate by dissolving niter cake in water and cooling the solution to −40°. H. M. Dawson[6] carries out the separation at −21°. At this temperature the residual solution is said to contain only 2.8 per cent sodium sulfate. From 10 tons of a 30 per cent acid niter cake he obtains 15 tons of Glauber's salt. If, however, the operation is carried out at 0°, 14 tons of this salt are obtained, while at +10° the yield is only 6.4 tons.

[10] Pascal, *Compt. rend.*, **164** (1917), 628; *Bull. soc. chim.*, **25** (1919), 35.

[11] U. S. Patent 1,258,895 (1918).

Contributions to Chemistry of Wood Cellulose[1]

I—Acetolysis of Spruce Pulp

By Louis E. Wise[2] and Walter C. Russell

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The work recorded in this paper is the beginning of an investigation of the chemical properties of wood cellulose as compared with those of cotton cellulose. This part of the work was done on spruce sulfite pulp, which yields appreciable amounts of cellobiose octacetate on acetolysis, as does cotton. Experimental evidence is presented that normal cellulose is the precursor of cellobiose octacetate, and normal spruce cellulose yields the same amount of the octacetate as does normal cotton cellulose under identical conditions of acetolysis. The authors therefore consider that Hibbert's formula may represent the constitution of normal spruce cellulose as well as that of normal cotton cellulose, and that their experiments present additional evidence that cellulose from the "lignocellulose" of wood and cotton cellulose may be identical.

NOTWITHSTANDING the recent important contributions to the chemistry of cotton cellulose,[3] the general term "cellulose" as applied to woods, straw, etc., remains a very vague one. The desirability of an exact definition of "wood cellulose" was recently pointed out by Dore[4] who states that the cellulose of woods "has been commonly accepted as a group designation, signifying a residue remaining after successive treatments with chlorine and dilute sodium sulfite solution, until free from lignin derivatives." A very similar definition has been assigned to wood cellulose by Schorger.[5]

Whereas this type of definition may act as a convenient stop-gap, and stimulate certain types of practical research, it seems to us to retard fundamental progress in the cellulose field. It is further open to the following very serious objections:

1—It defines as cellulose a mixture of varying composition, isolated by a convenient but arbitrary analytical procedure.

2—It is not based on any comparison of the chemical properties of the substance in question with those of a standard cotton cellulose.

3—It makes for confusion in the general usage of the term "cellulose."

Schorger[5] has shown in his very important series of analyses of some American woods, that there are wide variations in pentosan content in the so-called "wood cellulose." It is quite evident that if the above definition of the cellulose of woods is accepted, we face the unpleasant possibility of a different cellulose for every species of wood, and that even in the same species of wood the composition of the cellulose (always accepting the above definition) may depend on the period of growth, on slight modifications in the methods of isolation used, and even on the skill and experience of the analyst. When factors of this type enter into consideration, a definition becomes of very questionable scientific value.

It might be urged that wood cellulose would be better defined as a residue obtained by some such procedure as the one mentioned by Dore—with a correction applied for the pentosan and methylpentosan content of such a residue. In fact this appears to be the commonly accepted European practice. Such a procedure, however, furnishes no experimental data that would throw light on the similarity or dissimilarity between the chemical constitution of wood cellulose and cotton cellulose. Without such experimental evidence it would be quite futile to attempt a redefinition of "wood cellulose."

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[1] Presented before the Section of Cellulose Chemistry, at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Professor of Forest Chemistry.

[3] Hibbert, THIS JOURNAL, **13** (1921) 334.

[4] THIS JOURNAL, **12** (1920), 266.

[5] *Ibid.*, **9** (1917), 567.

The preliminary report of Herzog and Jancke[6] has a very important bearing on this subject. These investigators applied the Debye and Scherrer Röntgen spectrographic method to a study of purified cotton, wood cellulose, and ramie fiber. In all cases, the celluloses showed interference bands corresponding to a rhombic system of crystals, and the same axial ratio was noted in all cases.

The work of Heuser and Boedeker[7] is in substantial agreement with the hypothesis that *normal* wood and *normal* cotton cellulose are chemically identical. Wood cellulose, which had been purified by means of 17 per cent sodium hydroxide, was hydrolyzed with fuming hydrochloric acid by Willstätter and Zechmeister's[8] method. A control experiment was carried out with cotton cellulose. In both cases, the rate of hydrolysis to glucose was very nearly the same, and the maximum yield of glucose was reached 16.5 hrs. after peptization of the cellulose.

The object of our investigation was to obtain, if possible, further data that would indicate similarity or dissimilarity of the constitution of cotton and wood cellulose. Many recent fundamental investigations on cellulose serve to emphasize the importance of the acetolysis reaction when applied to cotton cellulose. The formation of cellobiose octacetate, while far from quantitative, has apparently a diagnostic value in indicating the presence of cellulose. As far as we know, cellobiose has not been obtained by the hydrolysis or acetolysis of polysaccharides other than cellulose.[9] Ost[10] has shown that, under conditions of protracted acetolysis, cotton yields up to 37 per cent of cellobiose octacetate. Madsen[11] showed that 30 to 32 per cent of the cellobiose octacetate could be obtained in a short time period. This yield could be increased up to 43 per cent of the theoretical yield by the saponification and subsequent re-acetolysis of the so-called dextrin acetates formed in the reaction. The recent investigations of Freudenberg[12] indicate that at least 61 per cent of the cotton cellulose molecule is composed of cellobiose residues.

Although the cellobiose octacetate reaction, as applied to cotton, has been rather carefully studied, and has been applied to filter paper of uncertain history, it has hitherto apparently never been applied to a cellulose isolated from wood in a comparative study. We have, therefore, used this reaction in our preliminary study of wood cellulose and have applied it primarily to spruce sulfite pulp, as the first step in an investigation of the chemical properties of wood cellulose as compared with those of cotton. Our experiments are being continued with cellulose isolated from other coniferous woods and from certain hardwoods.

EXPERIMENTAL PART

The method of acetolysis used in our work was essentially that of Klein[13] as modified by Madsen.[11] The material used was spruce sulfite pulp taken from a shipment sent to us through the courtesy of the Riordon Company, Ltd. Comparative experiments were made with surgical cotton, snipped into short threads. The pulp was shredded on a grater and screened through a 20-mesh sieve. Only those particles passing the sieve were used. The moisture content of the air-dried cotton was 5.3 per cent; that of the pulp 7.2 per cent.

In the acetolysis reactions, 5 g. of air-dried sample were very gradually incorporated into a cold mixture of 20 g. of redistilled acetic anhydride (b. p. 135° to 137° C.) and 5 g. of concentrated sulfuric acid, the mixture having been initially prepared at a temperature well below 10°. The elevation of temperature owing to the addition of the cellulose was also carefully controlled. The maximum temperature recorded in any of our experiments was 55°, but in this case the reaction mixture was immediately cooled to below 30°. In other cases, the highest temperature was 40° to 50° C., and here again cooling was resorted to. After liquefaction of the reaction mixture had set in, the solution was allowed to stand at 25° to 27° C. for 6 to 7 days. Crystallization normally began after 3 days, and at the end of the 6-day period, both the cotton and the spruce pulp had been converted into a stiff crystalline paste. The latter was treated with 30 cc. of glacial acetic acid, warmed to 50°, and immediately poured into 700 cc. of ice water. The white flocculent precipitate thus obtained, after standing for 0.5 hr., was filtered off on a Büchner funnel, washed with water until free from sulfates, and dried at 90° to 100°. It was then extracted with chloroform, the extract evaporated, and the residue dissolved in the minimum amount of boiling 95 per cent alcohol. The alcoholic solution in the case of the product derived from cotton was always clear. That derived from spruce, however, invariably yielded an opalescent solution at this point. In either case the alcoholic solution was treated with a small amount of boneblack, and the solution filtered through a hot water funnel (with water heated to about 80°). The filtrates were allowed to crystallize in an ice bath. The crystals, which appeared homogeneous under the microscope, were filtered off, and the filtrates evaporated to 50 to 75 cc. Small amounts of crystalline material could usually be recovered under these conditions. Further evaporation, however, caused the separation of a taffy-like resinous substance—no doubt the acetylated dextrins studied by Madsen. Melting-point determinations indicated that the crystalline product obtained from spruce was identical with that obtained from cotton. Both melted at 225.5° (uncorr.). In a preliminary experiment, cellobiose octacetate was prepared from filter paper by the method outlined by Haworth and Hirst.[14] In this case the substance also melted at 225.5° (uncorr.), and the melting point of this material mixed with that prepared from spruce pulp showed no depression. Madsen gives the melting point of cellobiose octacetate as 228° (corr.). The product obtained from spruce is thus shown to be cellobiose octacetate.

TABLE I—ANALYTICAL DATA ON MATERIALS USED (Dry basis)

PER CENT	COTTON	SPRUCE PULP
"Total cellulose" after single chlorination	98.1	96.2
"Total cellulose" after four chlorinations	96.9	94.7
"Normal cellulose" after treatment of original sample with NaOH (17.5%)	97.2	80.8
"Normal cellulose" after one chlorination	91.8	76.2
"Normal cellulose" after four chlorinations	83.5	68.7

In several of our experiments, the yields of cellobiose octacetate from cotton and from spruce pulp were determined as carefully as possible. Madsen's[15] highest yields of cellobiose octacetate were 5.8 to 6.2 g. from 10.0 g. of air-dried cotton. In our case the yield was 2.94 g. of the octacetate from 5 g. of air-dried cotton. In all cases, the yields of the octacetate from air-dried spruce pulp were appreciably lower than those from the same weight of air-dried cotton. These differences can best be discussed by reference to Table I, which gives some analytical data on the materials used, and to Table II, which gives yields of cellobiose octacetate.

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[6] *Ber.*, **53** (1920), 2162; through *C. A.*, **15** (1921), 1311.

[7] *Z. angew. Chem.* (Aufsatzteil), **34** (1921), 461.

[8] *Ber.*, **46** (1913), 2401.

[9] The "tunicin" of the tests of the ascidians (marine animals) yields cellobiose and is commonly accepted as being cellulose.

[10] *Ann.*, **398** (1913), 337.

[11] Dissertation, Hannover, **1917**, 16.

[12] *Ber.*, **54** (1921), 767.

[13] *Z. angew. Chem.*, **24** (1911), 1127.

[14] *J. Chem. Soc.*, **119** (1921), 197.

[15] We refer to Madsen's highest yields, excluding those experiments in which further treatment was applied to the "dextrin acetates" formed in the reaction.

TABLE II—COMPARISON OF YIELDS OF CELLOBIOSE OCTACETATE OBTAINED FROM COTTON AND FROM SPRUCE PULP

	COTTON	SPRUCE PULP
Anhydrous material used in acetolysis, grams..........	4.74	4 64
"Normal cellulose" after treatment of original sample with 17.5% NaOH, grams......	4.60	3.74
Cellobiose octacetate obtained, grams.............	2.942	2.149
Percentage of theoretical yield of octacetate calculated from normal cellulose content.....................	30.5	27.4

In the case of cotton the so-called "total cellulose" was determined by Sieber and Walters' method[16] (as outlined by Dore[4]). This involved four chlorinations and the results were somewhat, but not appreciably, lower than the amounts of "total cellulose" that could be obtained when only one chlorination (followed by the usual sodium sulfite treatment) was used. It is interesting to note, however, that the successive chlorinations seriously affect the amount of so-called normal (or α-) cellulose in the cotton (when determined by the Cross and Bevan mercerization test). The normal cellulose content is appreciably lowered by repeated chlorination—which might reasonably be expected in the case of a gradual oxidation of cellulose with the formation of alkali-soluble products. A very similar picture is presented in the case of the spruce pulp. The differences between the "total cellulose" in the case of cotton and spruce pulp are not very great (approximately 2 per cent). On the other hand, whereas very little of the original cotton is soluble in alkali, the original spruce pulp loses nearly 20 per cent when treated with 17.5 per cent NaOH, as shown in Row 3 of Table I.

It is evident that the "total cellulose" determination, while it gives a good index of the amount of cellulose that was present in the original sample (provided always this sample had not been subjected to oxidation prior to the analysis), does not necessarily indicate the actual amount of cellulose at the end of such an analysis. It certainly does not give a true index of the cellulose content of material, the previous history of which would indicate that it had been subjected to vigorous oxidation. These facts have been considered in calculating the percentage yield of cellobiose octacetate. Theoretically 1 g. of "pure" cellulose would yield (if complete conversion *could* take place) 2.09 g. of cellobiose octacetate. It would be obviously incorrect to assume that the original pulp and cotton were "pure" cellulose, and it would be unjustifiable to base our yield on the "total cellulose" determinations on the two samples. The so-called total cellulose would contain some material in which (assuming Hibbert's formula) the alcoholic hydroxyl groups had been oxidized, and such material would not yield cellobiose octacetate on acetolysis. Since the object of our experiments was that of a comparative study, it appeared best to have our yields based on the "normal" cellulose content of both the cotton and the spruce pulp. In formulating a working hypothesis we considered as normal cellulose that residue which remained after treatment with 17.5 per cent alkali without previous chlorination or sulfite digestion. Although this might appear to be an arbitrary assumption, it is more logical than one which takes as normal cellulose a residue obtained after one or more successive chlorinations. The assumption appeared justified, since the original cotton sample after chlorination gave no coloration with sodium sulfite, and since the coloration in the case of spruce pulp was very slight. This would indicate the presence of only small amounts of lignin. Assuming that the normal cellulose was in each case the precursor of cellobiose octacetate, it appears from Table II that the yields of octacetate from normal spruce cellulose and from normal cotton cellulose are not so very different.

EXPERIMENTS ON NORMAL CELLULOSE—A series of experiments were then undertaken with a view toward testing our working hypothesis. *"Normal cellulose"* from cotton and spruce pulp was actually prepared and acetolyzed. Snipped surgical cotton and grated spruce pulp were treated with a 17.5 per cent solution of sodium hydroxide, allowed to stand 0.5 hr., and subsequently washed with successive portions of water and dilute acetic acid, and finally washed until the rinsings were no longer acid. Each sample was then allowed to dry in air. The moisture content of the normal cotton cellulose thus obtained was 7.5 per cent; that of the normal wood cellulose was 7.8 per cent. The normal cotton cellulose contained 1.18 per cent pentosans; the normal spruce cellulose contained 1.25 per cent pentosans.

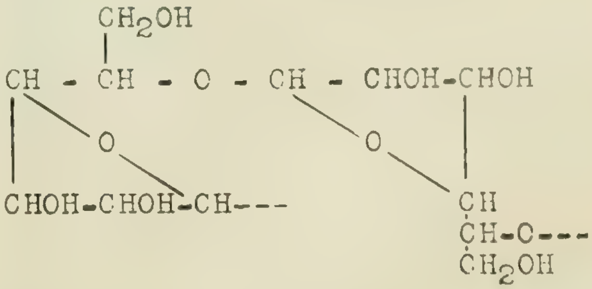
Five-gram portions of the normal cellulose (from cotton or wood) were acetolyzed by the method already outlined, with but few modifications. In one set of experiments (A, Table III) the acetolysis mixtures were heated for 2 hrs. at 40° to 50°, and were allowed to stand 8 days at 15° to 20°. The other acetolysis mixtures (B, Table III) were similarly heated, but were allowed to stand at room temperature for 17 days.

TABLE III—YIELDS OF CELLOBIOSE OCTACETATE FROM NORMAL COTTON AND NORMAL SPRUCE CELLULOSE, CORRECTED FOR PENTOSAN CONTENT

	NORMAL COTTON CELLULOSE		NORMAL SPRUCE CELLULOSE	
	Set A	Set B	Set A	Set B
Anhydrous normal cellulose (corrected for pentosan content), grams...............	4.571	4.571	4.552	4.552
Cellobiose octacetate yield, grams.....................	2.6976	2.7340	2.6634	2.7290
Cellobiose octacetate based on the theoretical yield, per cent.....................	28.2	28.6	28.0	28.7
Melting points of samples of cellobiose octacetate isolated (uncorr.)............	226°	226°	227.5°	227°

The crude octacetate was crystallized from 95 per cent ethyl alcohol, without preliminary extraction with chloroform. The yields given in Table III refer to the crystalline product thus obtained. Emphasis should be placed on the fact that very nearly identical conditions were maintained in each set of acetolysis experiments. While the maximum yield of cellobiose octacetate was never reached, the results in each set are strictly comparable.

It is evident from these experiments that the grouping



occurs not only in cotton but also in the cellulose of spruce wood, and there is every evidence that the amounts of cellobiose that may be obtained by using a definite procedure in the acetolysis of either normal cotton or normal spruce cellulose are very nearly the same. It is, therefore, highly probable that Hibbert's formula[3] for cellulose applies equally as well to the normal cellulose obtained from spruce wood as it does to cotton cellulose.

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[16] *Papier-Fabr.*, **11** (1913), 1179.

Iodine and Bromine Values of Petroleum Products[1]

By E. M. Johansen[2]

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In view of the results of the work described in this paper it may be concluded that iodine values obtained with Hanus, Wijs, or Hubl solutions are not indicative of the comparative unsaturation of petroleum products, because they represent not only the halogen which is added to the double bond but also that which substitutes in the hydrocarbons. This paper records iodine and bromine values of a number of petroleum products, as well as the relative quantities of halogen substituted and added. When two reactions take place simultaneously, low results are obtained. Changes in bromine and iodine value which occur when the ratio of sample to halogen is changed, or when time or temperature of reaction is varied, are largely due to changes in the substitution reaction.

No fixed relation has been found between bromine and iodine values of petroleum products. Although the bromine-iodine solution keeps its strength better and is more convenient to handle than the bromine solution, the latter is recommended for general use. The bromine-iodine solution often gives uncontrollable reactions during titration which produce misleading results.

A bibliography of the literature dealing with the iodine and bromine values of petroleum products is appended.

When the iodine or bromine absorption values of petroleum products are determined, hydrogen halide is often liberated as the result of substitution reactions. Few investigators have taken this phase of the reaction into account. In the majority of the cases, the total amount of combined halogen has been used for the calculation of the absorption numbers, and these have been used as indications of the relative "unsaturation" of the materials examined.

The present work was undertaken with a view to ascertaining what correction should be made in the ordinary iodine and bromine absorption numbers to allow for the substituted halogen. This involved the determination of the amount of hydrogen halide formed during the reactions. Since the ordinary Hanus and Wijs solutions do not permit these determinations, a carbon tetrachloride solution was used. This contained the same amounts of halogens as the Hanus solution, *i. e.*, 13.2 g. of resublimed iodine and an equivalent amount of bromine, in 1000 cc. of solution. It was found that the halogens in the solution must be strictly equivalent, if good checks were to be obtained. The solution was very permanent, if kept in bottles of dark glass. The bromine solution used in the investigations was a 0.2 N solution of bromine in carbon tetrachloride. It was somewhat likely to lose strength by evaporation of bromine, but in these respects it was better than the 0.33 N solution of bromine used by several investigators.

Method of Determining Absorption

Exactly 5 g. of the sample were dissolved in carbon tetrachloride. The solution was transferred to a 50-cc. flask, diluted to the mark with carbon tetrachloride, and mixed well. In the case of volatile substances that could not be weighed without loss, the specific gravity was ascertained and a volume corresponding to 5 g. was introduced into carbon tetrachloride from a buret, the tip of which was introduced below the surface of the tetrachloride. Ten cc. of the 50 cc. of dilute solution were carefully introduced from a buret into the reaction flask, and exactly 25 cc. of the halogen solution were added from another buret. A blank containing 10 cc. of carbon tetrachloride and 25 cc. of the halogen solution was prepared in another flask, which was stoppered immediately after the introduction of the halogen solution.

The reaction flasks were Erlenmeyer flasks of about 250-cc. capacity, each provided with a rubber stopper carrying a 125-cc. separatory funnel. Immediately after the halogen solution had been introduced the flask was closed by the stopper carrying the funnel, the stopcock of the latter was closed, and the flask with contents was placed in a bath, kept at 20° C., for the required length of time (0.5 hr.). During this time, the flask was protected against the light by a cover. Next, 10 cc. of potassium iodide solution (containing 15 g. KI in 100 cc.) and 100 cc. of freshly boiled distilled water, cooled to room temperature, were introduced into the funnel. The flask was immersed in ice water, and by careful opening of the stopcock, some of the contents of the funnel was allowed to enter the flask and absorb the hydrogen halide vapors. When no more water entered the flask, even upon repeated gentle shaking of the latter, the vapors were absorbed. The stopper and funnel were removed and the liquid remaining in the funnel was run into the flask.

The quantity of free halogen remaining in the flask after the reaction was titrated in the usual way with 0.1 N sodium thiosulfate solution, with the addition of a few drops of a freshly prepared solution of soluble starch as indicator at the end of the titration. For convenience in shaking during the titration, an ordinary ground-glass stopper was substituted for the stopper carrying the separatory funnel.

The hydrogen halide present was determined according to McIlhiney's method by titration with 0.1 N sodium thiosulfate solution after adding 4 cc. of a solution of potassium iodate, containing 4 g. KIO_3 in 100 cc. The blank was titrated in the same manner.

In the case of the bromine-iodine solution, one blank was found sufficient for several tests, if the temperature of the laboratory remained constant. For the bromine solution it was necessary to run one blank for each test. The best way to run a blank on the bromine solution was to introduce 100 cc. water, 10 cc. KI solution and 10 cc. carbon tetrachloride into the flask, add the 25 cc. bromine solution, and immediately close the flask.

From the differences between the titrations of the blank and those of the reactions were found:

A = Total amount of halogen absorbed (expressed as iodine or bromine),

B = Amount of halogen present as hydrogen halide at the time of the titration. If the latter amount was assumed to be equal to that combined by substitution, then

A−2B = Halogen combined by addition, and

B = Halogen combined by substitution.

These quantities were calculated in per cent of the amount of material examined, and the results were recorded as "addition value" and "substitution value."

The use of 1 g. of substance for examination was found satisfactory in the case of ordinary uncracked petroleum products. Products containing larger amounts of unsaturated substances were examined by using 0.5 g. in 10 cc.

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[1] Presented before the Section of Petroleum Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Research Chemist.

solution, while in the case of highly cracked materials (pressure-still gasolines, etc.), a ratio of 0.125 to 0.250 g. to 10-cc. solution was found necessary. The use of 10 cc. of solution was found important if comparable results were desired. If the volume of solvent was decreased, the results obtained were somewhat higher, while if a greater volume of solvent was used, lower results were obtained.

COMPARISON WITH HANUS METHOD

A series of determinations of iodine absorption values was made upon a number of petroleum products and fatty oils, with the object of comparing the values found with Hanus solution with those obtained when the new solution was used. The results are given in Table I.

TABLE I—COMPARISON OF IODINE VALUES OF PETROLEUM PRODUCTS AND FATTY OILS

A = addition; S = substitution; A + 2S = total

	Grams Oil Used	CCl₄ Solution A	CCl₄ Solution S	CCl₄ Solution A + 2S	Hanus Solution Total
Straight run lamp oil distillate	1	2.40	3.70	9.80	9.26
Cracked lamp oil distillate	1	8.69	9.26	27.21	26.35
Uncracked gas oil	1	5.36	12.32	30.00	25.71
Cracked gas oil	1	8.30	13.26	34.82	30.26
White Rose lubricating oil	1	1.43	8.90	19.23	17.09
180 pale neutral oil	1	1.81	11.18	24.17	20.48
Batching oil	1	0.13	11.40	22.93	19.59
Solar red oil	1	0.00	11.11	22.22	19.83
White medicinal oil	1	0.43	0.00	0.43	0.37
Neat's-foot oil	1	..	...	53.46	59.87
Lard oil	1	..	...	54.80	60.16
Lard oil	0.5	..	...	54.91	59.86
Sperm oil	0.5	..	...	80.56	80.66
Tallow oil	1	..	...	53.35	60.31
Olive oil	0.5	..	...	82.13	82.33
Rape oil	0.5	..	...	87.24	88.38
Sesame oil	0.5	..	...	94.79	97.73
Soy-bean oil	0.2	.	...	127.47	127.99
Boiled linseed oil	0.2	..	...	171.23	175.94
Whale oil	0.2	..	...	102.56	106.30

The total per cent of halogen absorbed by each petroleum product from the new solution was higher than that absorbed from the Hanus solution. The results also showed that the total iodine absorption values found by the Hanus or other methods were unsuitable as an indication of the comparative unsaturation of petroleum products.

The relations between the iodine values of the fatty oils as found by the two solutions were irregular. The Hanus values were generally slightly higher than those obtained by aid of the new solution.

TABLE II—DUPLICATE DETERMINATIONS OF IODINE VALUES OF PETROLEUM PRODUCTS

(1-gram samples used)

	A	S	A + 2S
Cracked lamp oil distillate	8.49	10.38	29.25
Cracked lamp oil distillate	8.32	10.45	29.22
Pennsylvania gas oil	1.43	13.06	27.55
Pennsylvania gas oil	1.84	12.79	27.42
Mid-continent gas oil (cracked)	7.31	11.10	29.51
Mid-continent gas oil (cracked)	7.31	11.10	29.51
Stock for paraffin oils	2.87	10.32	23.51
Stock for paraffin oils	3.13	10.19	23.51
Neutral lubricating stock	0.73	9.46	19.65
Neutral lubricating stock	0.78	9.40	19.58
Filtered lubricating oil	0.65	11.88	24.41
Filtered lubricating oil	0.52	11.88	24.28
120° m. p. paraffin wax	0.44	0.40	1.24
120° m. p. paraffin wax	0.71	0.40	1.51

ACCURACY

The degree of accuracy of the new method was investigated. A number of petroleum products were examined on two different days by two analysts, who had had no previous experience in the work. The results recorded in Table II indicate that a high degree of accuracy is attainable when using the new method.

TESTS ON FRACTIONATED OILS

Two samples of crude oils were carefully fractionated by distillation, using steam to prevent cracking. The iodine and bromine values of the crude oils and the fractions were determined on 1-g. samples. The results are shown in Table III.

It was concluded from the results, that although the total per cent of halogen absorbed increased rapidly with increasing boiling points of the fractions, this increase was mainly due to increase in substitution. The addition values did not change to such an extent. No constant relations were found between the iodine and bromine values of the same fraction.

TESTS ON TYPICAL PETROLEUM PRODUCTS

The values obtained with certain typical petroleum products are tabulated in Table IV.

TABLE IV—IODINE AND BROMINE VALUES OF TYPICAL PETROLEUM PRODUCTS

	Grams Used	Iodine Value A	Iodine Value S	Iodine Value A+2S	Bromine Value A	Bromine Value S	Bromine Value A+2S
Pentane	1	0.37	...	0.37	0.39	0.06	0.51
Straight run naphtha	1	0.53	1.58	3.69	0.65	1.55	3.75
Straight run naphtha (treated)	1	0.47	1.14	3.29	0.64	1.44	3.52
Cracked naphtha	1	14.70	8.16	31.02	9.39	4.62	18.63
Cracked naphtha (treated)	1	10.72	8.48	27.68	6.80	5.65	18.10
Straight run lamp oil distillate	1	1.32	5.04	11.40	0.69	3.13	6.95
Straight run lamp oil distillate (treated)	1	0.74	5.06	10.86	0.48	3.00	6.48
Cracked lamp oil distillate	0.5	23.23	9.52	42.27	21.81	7.57	36.95
Cracked lamp oil distillate (treated)	0 5	17.59	10.63	38.85	16.42	8.57	33.56
Straight run gas oil	1	2.56	9.62	21.80	2.44	3.93	10.30
Cracked gas oil	1	4.59	14.26	33.11	4.45	7.22	18.89
Lubg. stock (uncracked)	1	0.83	12.06	24.95	2.09	5.83	13.75
Lubg. stock (uncracked, filtered)	1	0.32	11.48	23.28	1.55	5.78	13.11
Lubg. stock (from run to coke)	1	0.85	14.43	29.71	3.55	9.48	22.51
Lubg. stock (from run to coke, treated)	1	0.42	13.32	27.06	1.39	7.17	15.73
26½ cylinder stock (Pa.)	1	2.29	10.99	24.27	1.76	6.43	14.62
26½ cylinder stock (filtered)	1	0.21	11.67	23.55	0.64	6.56	13.76
Petrolatum stock	1	11.31	7.26	25.83	6.93	3.10	13.13
Petrolatum stock (filtered, U. S. P.)	1	1.76	11.31	24.38	2.43	4.40	11.23
Refined paraffin wax (132° m. p.)	1	1.10	...	1.10	1.16	2.25	5.66
Amorphous wax from petrolatum (165° m. p.)	1	1.32	2.90	7.12	1.38	1.50	4 38
White medicinal oil	1	0.05	. .	0.05	0.40	1.90	4.20
86–88 gasoline	1	1.74	0	1.74	0.58	0.34	1.26
70 gasoline	1	1.20	0	1.20	0.83	0.05	0.93
Motor gasoline	1	5.91	2.73	11.37	3.71	1.15	6.01
V. M. & P. naphtha (55° Bé.)	1	2.00	2.51	7.02	1.47	1.10	3 67
Varnoline (51° Bé.)	1	2.63	3.36	9.3	1.49	0.85	3.19

TABLE III—IODINE AND BROMINE VALUES OF CRUDE PETROLEUM OILS AND THEIR FRACTIONS (1-gram samples used)

	Pennsylvania Crude								Somerset (Ky.) Crude							
			Iodine Value			Bromine Value					Iodine Value			Bromine Value		
FRACTION	Per cent by Volume	° Bé.	A	S	A+2S	A	S	A+2S	Per cent by Volume	° Bé.	A	S	A+2S	A	S	A+2S
Crude	..	43.3	2.87	7.40	17.67	2.64	2.82	8.28	..	36.9	3.16	9.77	22.70	3.65	4.24	12.13
1	5	76.8	2.14	0.60	3.34	1.04	0.76	2.56	10	69.7	2.76	1.23	5.22	2.45	0.40	. 3.25
2	10	65.2	2.59	0.94	4.47	1.42	0.80	3.02	10	56.6	3.97	3.77	11.51	3.18	1.16	5.50
3	10	56.8	2.99	2.62	8.23	1.87	1.04	3.95	10	50.1	4.11	5.08	14.27	3.39	1.65	6 69
4	10	51.9	3.29	3.73	10.75	2.16	2.60	7.36	10	43.5	4 23	7.10	18.43	3 34	2.58	8.50
5	10	46.7	3.25	4.88	13.01	2.00	3.17	8.34	10	38.5	3.72	8.71	21.14	3 26	3.35	9.96
6	10	42.3	3.07	6.28	15.63	1.89	4.19	10.27	10	34.6	3 11	9.94	22.99	3.20	4.42	12.04
7	10	38.1	2.88	7.80	18.48	2.21	3.72	9.65	10	30.3	3 16	10.92	25.00	3.17	5 43	14.03
8	10	34.3	2.34	9.68	21.70	2.49	4.52	11.53	10	26.7	2.19	12.56	27.31	3.13	7.33	17.79
9	10	31.4	1.88	10.97	23.82	2.23	4.77	11.77						...	.	22 24
Residue	15	26.2	1.66	12 97	26.60	2.47	6.35	15.17	20	17 5	2.76	15 94	34.64	2 08	10 08	.
AVERAGE	..	....	2.56	6.90	.....	2.08	3.61	.....	..	....	3.38	9.39	.....	2.91	4.90	.....

The results confirmed those found with the fractions of the crude oils; *i. e.*, no general relation between the bromine and iodine values of the oils could be derived. It was noticed that in many cases the tendency towards formation of substitution compounds was greater in the case of the bromine-iodine solution.

It may be possible that the presence of iodine increases the tendency of the bromine to form substitution compounds. It was noticed that, when substances gave a high substitution value with the bromine-iodine solution, the brownish color of the latter changed during the reaction to violet or the color of a solution of iodine in carbon tetrachloride.

A few other substances were examined. The results are given in Table V.

TABLE V—IODINE AND BROMINE VALUES OF VARIOUS HYDROCARBONS AND MINERAL OILS

	Grams	Iodine Value			Bromine Value		
	Used	A	S	A+2S	A	S	A+2S
Cetene, impure	0.25	90.45	4.49	99.43	56.25	3.98	64.21
Cetene, purified	0.25	104.60	0.19	104.98	66.00	1.12	68.24
Turpentine	0.125	182.81	23.12	229.05	140.65	55.45	251.55
Xylene	1	0.90	3.11	7.12	0.77	16.89	34.55
Naphthalene	1	0.22	3.58	7.38	2.67	0.11	2.89
Texas lubricating oil (contained naphthenic acids)	1	−2.26	13.23	24.20	0.25	7.63	15.51
Brownlee lubricating oil (1.5 g. KI in 110 cc. solution added at titration)	0.25	−22.72	74.64	126.56	−1.98	39.92	77.86
Brownlee lubricating oil (16.5 g. KI in 110 cc. solution added at titration)	0.25	−14.02	70.20	126.38	1.16	38.10	77.36
California lubricating oil (contained naphthenic acids)	1	−1.28	13.33	25.38	...	...	...
California lubricating oil (acids removed)	1	0.30	12.50	25.30	...	...	...

Of these, the most interesting was the Brownlee lubricating oil, a material produced by polymerization of unsaturated substances. This was a very good example of an oil having a "negative addition value." Certain oils, such as reduced lubricating stocks, Texas and California lubricating oils, and others, showed this peculiarity, which generally appeared to be much more pronounced in the case of the iodine addition. A negative value of bromine addition was found only in the case of the Brownlee lubricating oil.

EXCESS ACIDITY

The method of determining the addition halogen, *i. e.*, by subtracting double the amount of the halogen found as hydrogen halide by the second titration, from the total amount of combined halogen, has the disadvantage that iodine liberated during this titration by any other acid present will be counted as due to hydrogen halide formed by substitution. The substitution value will be found too high, and the addition value too low, as the total absorbed halogen is not affected. If the amount of other acids present is large enough, the addition value may become zero, or even negative, as in the case of the Brownlee oil.

The sources of this excess acidity may be organic acids present in the petroleum product, or hydrogen halide acids resulting from the hydrolysis of halogen compounds formed during the reaction. Such hydrolysis may take place upon addition of the water before the titration.

Investigations have shown that the organic acids present in petroleum products are not able to liberate iodine from an aqueous solution of potassium iodide and iodate. By introduction of halogen into such acids, their negative character may be so intensified that they readily liberate iodine from the solution. Oils containing naphthenic acids did not liberate iodine from the solution, but gave negative iodine addition values. After removal of the naphthenic acids, the iodine addition values became positive.

TABLE VI—CHANGES IN IODINE AND BROMINE VALUES WITH CHANGES IN AMOUNT OF MATERIAL USED

	Grams	Iodine Value			Bromine Value		
OIL	Used	A	S	A+2S	A	S	A+2S
Pressure-still distillate	1	20.07	9.25	38.57	17.04	5.61	28.26
	0.75	21.76	12.93	47.62	16.94	6.09	29.12
	0.5	22.16	17.17	56.50	16.08	7.38	30.84
	0.125	20.81	23.81	68.43	16.28	8.70	33.68
Tube-cracked naphtha	0.75	45.37	9.03	63.43	....	...	...
	0.5	66.04	12.58	91.20	60.52	8.21	76.94
	0.25	109.46	22.01	153.48	70.53	12.21	94.95
	0.13	120.32	26.35	173.02	71.87	12.86	97.59
Cracked lamp oil	1	9.20	9.24	27.68	7.15	6.87	20.89
	0.75	9.34	10.50	30.34	6.76	8.32	23.40
	0.5	9.54	12.34	34.22	6.64	7.44	21.52
	0.25	9.84	14.39	38.62	6.45	6.92	20.29
Filtered lubricating oil	1	0.91	11.17	23.25	1.47	5.26	11.99
	0.75	1.16	12.47	26.10	1.23	5.27	11.77
	0.5	1.21	14.54	30.29	1.14	5.40	11.94
	0.25	1.36	16.51	34.38	1.32	6.25	13.82
Paraffin oil	1	0.34	10.86	22.06	1.41	5.09	11.59
	0.75	0.40	12.97	26.34	1.35	5.56	12.47
	0.5	0.52	14.22	28.96	1.20	6.04	13.28
	0.25	0.59	16.02	32.63	0.94	8.11	17.16
Uncracked gas oil	1	2.54	8.11	18.76	2.01	3.55	9.11
	0.75	2.63	9.24	21.11	2.12	4.32	10.76
	0.5	2.72	10.22	23.16	2.08	5.44	12.96
	0.25	2.88	11.66	26.20	2.08	5.68	13.44
Pa. cylinder stock	1	2.70	10.11	22.92	2.58	4.55	11.68
	0.75	1.93	11.65	25.23	2.42	4.66	11.74
	0.5	0.60	13.43	27.46	2.36	4.96	12.28
	0.25	0.30	14.97	30.24	2.36	5.58	13.52
"Brownlee" lubricating oil	1	−2.91	19.13	35.35	−1.50	19.44	37.38
	0.75	−6.97	26.46	45.95	−0.54	25.46	50.38
	0.5	−11.66	38.00	64.34	−1.65	30.92	60.19
	0.25	−25.76	75.44	125.12	−1.94	39.40	76.86

It appeared very probable that the presence of hydrogen halide, formed by hydrolysis of halogen compounds, was the cause of negative addition values in certain cases. In

TABLE VII—INFLUENCE OF QUANTITY OF MATERIAL UPON IODINE ADDITION AND SUBSTITUTION VALUES

Olefin—White Oil Mix, 1 g. (High Addition Value)					Mineral Oil—White Oil Mix, 1 g. (Substitution Value)					Olefin—Mineral Oil Mix, 1 g. (Addition and Substitution Values)							
												Iodine Value Found			Iodine Value Calculated		
Grams Olefin in 1 Gram Mixture	A	S	A+2S	Iodine Value of Olefin	Grams Mineral Oil in 1 Gram Mixture	A	S	A+2S	Iodine Value of Mineral Oil	Grams Olefin in 1 Gram Mixture	Grams Mineral Oil in 1 Gram Mix.	A	S	A+2S	A	S	A+2S
0.5	52.13	0	52.13	104.26	0	0.19	0	0.19	...	...	...	...	...	...	...	...	...
0.4	41.04	0.31	41.66	104.15	0.6	0.21	9.22	18.65	31.08	0.4	0.6	40.46	3.96	48.38	41.25	9.53	60.31
0.3	30.76	0.29	31.34	104.47	0.7	0.23	9.90	20.03	28.61	0.3	0.7	30.52	5.68	41.88	30.99	10.19	51.37
0.2	21.04	0.06	21.16	105.60	0.8	0.11	10.31	20.73	25.91	0.2	0.8	19.80	7.81	35.42	21.15	10.37	41.89
0.1	10.82	0	10.82	107.70	0.9	0.12	11.57	23.26	25.84	0.1	0.9	9.74	9.92	29.58	10.94	11.57	34.08
0.05	5.37	0	5.37	106.40	0.95	0.07	11.82	23.71	24.96	0.05	0.95	4.07	11.27	26.61	5.44	11.82	29.08
0	0.05	0	0.05	....	1	0.05	12.31	24.67	24.67	...	...	...	...	...	...	...	...

TABLE VIII—INFLUENCE OF TIME UPON IODINE VALUES

	0.5 Hr.			1 Hr.			2 Hrs.			4 Hrs.		
	A	S	A + 2S	A	S	A + 2S	A	S	A + 2S	A	S	A + 2S
Gas oil	5.37	11.93	29.23	5.40	12.25	29.90	5.48	12.94	31.36	5.56	13.34	32.24
Paraffin oil	0.30	10.45	21.20	0.34	11.27	22.88	0.41	12.13	24.67	0.49	12.73	25.95
Neutral lubricating distillate	2.25	8.35	18.95	2.51	8.80	20.11	2.66	9.19	21.04	3.37	9.70	22.77
Filtered lubricating oil	0.86	11.10	23.06	0.98	11.65	24.28	1.09	12.14	25.37	1.16	12.81	26.78
Pressure-still distillate	19.40	9.81	39.02	19.03	10.11	39.25	18.61	10.45	39.51	18.09	10.90	39.89
Cetene, purified	104.25	0	104.25	104.56	0.08	104.72	104.31	0.16	104.63	...	...	...

TABLE IX—INFLUENCE OF TIME UPON IODINE AND BROMINE VALUES

Time at 20° C. Hrs.	Olefins—White Oil Mix (Addition Value)						Mineral Oil (Substitution Value)					
	Iodine Value			Bromine Value			Iodine Value			Bromine Value		
	A	S	A+2S	A	S	A+2S	A	S	A+2S	A	S	A+2S
0.25	19.91	0.44	20.79	13.07	0.14	13.35	0.61	10.40	21.41	1.09	4.61	10.31
0.5	19.94	0.44	20.82	12.91	0.25	13.41	0.74	11.26	23.26	0.98	5.19	11.36
1	19.96	0.55	21.06	13.13	0.37	13.87	0.38	11.40	23.18	0.84	5.49	11.82
2	20.18	0.49	21.16	13.37	0.49	14.35	1.06	12.45	25.96	0.75	6.21	13.17
4	20.22	0.61	21.44	13.65	0.59	14.83	1.78	13.28	28.34	0.44	6.67	13.78
16	20.29	1.02	22.33	13.43	0.73	14.89	0.53	13.75	28.03	1.05	8.04	17.13

TABLE X—INFLUENCE OF TEMPERATURE UPON IODINE AND BROMINE VALUES

TEMP. ° C.	Olefin—White Oil Mix (Addition Value)						Mineral Oil (Substitution Value)					
	Iodine Value			Bromine Value			Iodine Value			Bromine Value		
	A	S	A+2S	A	S	A+2S	A	S	A+2S	A	S	A+2S
15	20.09	0.45	20.99	12.79	0.19	13.17	0.78	11.00	22.78	0.57	4.90	10.37
20	20.00	0.41	20.82	12.95	0.25	13.45	1.04	11.18	23.40	0.97	5.02	11.01
25	20.14	0.44	21.02	12.96	0.36	13.68	0.64	11.17	22.98	1.26	5.25	11.76

this case, decrease in the amount of water added before the titrations, or a substitution of concentrated potassium iodide solution for the water, should lower the ratio of hydrolysis of the compounds, and the amount of acid formed. This was found by experiments to be the case, the negative values disappearing to some extent.

The occurrence of negative iodine values is the great drawback to the use of the bromine-iodine solution for the examination of petroleum products. It is impossible to know without doubt when a reaction of this character takes place, with a too low addition value as a consequence. It has, however, been noticed that when hydrolysis takes place, the end-point of the second titration is not sharp, but that the blue color of the solution returns persistently after every addition of sodium thiosulfate solution.

SIZE OF SAMPLE

It is well known that, if the relation between the amount of material examined and the quantity of halogen present is changed, the halogen absorption found will vary. Generally, the lower the ratio of material to halogen, the higher the absorption value. A number of petroleum products were examined, by taking 25 cc. of bromine solution or the same volume of the bromine-iodine solution, and varying quantities of the substances, dissolved in carbon tetrachloride and diluted to 10 cc. The results showed that the increases in the absorption were caused mainly by increased substitution reactions. The addition values were relatively little changed. The bromine values in general showed less differences than the iodine values. The results can be found in Table VI.

For further study of this subject, a mineral oil was produced which had a very low addition value with a fairly high substitution value. Also, an olefin was prepared with a very low substitution value and a high addition value. Mixtures of definite proportion of these oils with an oil having a very low total iodine value (white medicinal oil) were prepared, as well as mixtures of the two oils in varying proportions. The iodine values of these mixtures were determined on 1-g. samples (Table VII).

The iodine value of the olefin varied relatively little, even if the quantity of material used for the determination was varied from 0.05 to 0.5 g. The iodine absorption of the mineral oil, which was mainly due to substitution reaction, varied much more within a narrower limit of amount used. In the mixtures of the two oils, the mutual influence of the iodine addition and substitution could be noticed.

EFFECT OF TIME

Bromine and bromine-iodine solutions were allowed to act upon petroleum products for varying lengths of time, and the amounts of halogen absorbed were determined. The same determination was repeated upon a mixture of an olefin and white medicinal oil, as well as a mineral oil of low addition value and relatively high substitution value. The results, from which it appeared that the substitution value was more changed than the addition value by lengthening the time of reaction, are compiled in Tables VIII and IX.

EFFECT OF TEMPERATURE

The iodine and bromine values of the oils reported in Table IX were also determined after allowing the reactions to take place at temperatures varying ± 5° C. from the normal temperatures (20° C.). The differences in the values were very slight when the bromine-iodine solution was used; greater differences occurred when the bromine solution was used. The results were tabulated in Table X.

BIBLIOGRAPHY

IODINE VALUES

Akunianz: Iodine values (Hubl) of crude oil. *Chem. Ztg. Repertorium*, **1896**, 1892; **1897**, 308.

Schidow: Iodine values (Hubl) of fractions from crude oil. *Chem. Ztg. Repertorium*, **1898**, 251.

Shinichi Takano: Iodine values of Japanese crude oil (by a 0.1 *N* solution of iodine in chloroform). *Intern. Petroleum Congr.*, **1900**, 60.

Salome: Iodine values (Hubl) of petroleum fractions boiling below 260° C. *Chem.-Ztg.*, **1902**, 224.

Krepelka: Iodine values (method not given) of petroleum pitches. *Inaugural Dissertation, Zurich*, **1904**.

Utz: Iodine values (Hubl-Waller) of lamp oils. *Z. Petroleum*, **1** (1905), 475.

Graefe: Iodine values (Hubl-Wijs) of crude oils, gasoline, lamp oils and gas oils. *Z. Petroleum*, **1** (1905), 12, 631.

Marcusson: Iodine values (Hubl-Wijs, Hubl-Waller) of lamp oils and lubricating oils. *Z. Petroleum*, **2** (1906), 798; *Chem.-Ztg.*, **1911**, 729.

Holde: Iodine values (Hubl) of lamp oils. "Untersuchung der Mineralöle," 2nd edition, 354.

Dreyfus: Iodine values (Hubl-Waller, Hanus) of paraffin oils. *J. Am. Leather Chem. Assoc.*, **3** (1908), 354.

Istrati and Mihailescu: Iodine values (Hubl) of paraffin wax. *C. A.*, **6** (1912), 1844.

Marcusson and Meyerheim: Iodine values (Hubl) of paraffin wax. *C. A.*, **6** (1912), 1844.

Radcliffe and Polychronis: Iodine values (Hubl, Wijs, Hanus) of transformer oils and lubricating oils. *J. Soc. Chem. Ind.*, **35** (1916), 340.

Smith and Tuttle: Iodine values (Hanus) of lubricating oils. *Bur. Standards, Tech. Paper* **37** (1917).

Dean and Hill: Iodine values (Hanus) of gasolines. *Bur. Mines, Tech. Paper* **181** (1917).

Roederer: Iodine values (Hubl-Waller, Wijs) of lignite tars and distillates. *Z. angew. Chem.*, **33** (1920), **1**, 235.

Espy: Iodine values (method not mentioned) of fractions of Cushing crude. Hamor and Padgett, "The Examination of Petroleum," 327.

BROMINE VALUES

McArthur: Bromine values (Br in CS_2) of naphtha, lubricating oils and paraffin wax. *J. Soc. Chem. Ind.*, **1888**, 64.

Allen: Bromine values (Br in CS_2) of various petroleum products. Redwood, "Petroleum," 1st edition, II, 617.

De Hailes: Bromine values (method not mentioned) of crude oils. Redwood, "Petroleum," 3rd edition, I, 253.

McIlhiney: Bromine values (determination of addition and substitution values) of heavy naphthas, neutral oils, paraffin. *J. Am. Chem. Soc.*, **21** (1899), 1084.

Mabery: Bromine values (Allen's method) of crude oils. *Am. Chem. J.*, **18** (1896), 215; **19** (1897), 796; **31** (1904), 16; **32** (1904), 185; **36** (1906), 266.

Richardson: Bromine values (method not mentioned) of petroleum residues. Allen, "Commercial Organic Analysis," 4th edition, III, 93.

Weger: Bromine values (titration with an aqueous solution of KBr and $KBrO_3$) of lamp oils. *Z. Petroleum*, **2** (1906), 101.

Utz: Bromine values (same method as Weger) of lamp oils. *Z. Petroleum*, **2** (1906), 43.

Graefe: Bromine values (same method as Weger) of lamp oils. *Z. angew. Chem.*, **19** (1906), 1580.

Routala: Bromine values (same method as Weger) of mixes of gasoline with amylene, etc. *Chem. Zentr.*, **1912**, II, 638.

Dean and Hill: Bromine values (McIlhiney) of gasolines. *Bur Mines, Tech. Paper* **181** (1917).

Grun and Wirth: *Z. angew. Chem.*, **33** (1920), 295.

Time and Concentration Factors in the Combination of Tannin with Hide Substance[1,2]

I—Gambier. II—Quebracho

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Despite the fact that vegetable tanning is the oldest tanning process known, there are no scientific data concerning the mechanism of the fixation of tannins by hide protein, or the factors which greatly influence the rate and degree of combination. The data given in this paper constitute a beginning in the study of this reaction, and while in themselves they do not serve for interpretation of the mysteries of the complex reactions involved, it is hoped that after a few years' experimentation sufficient information will be accumulated to clarify the reactions and aid us in a more intelligent control of vegetable tanning.

It can be said that while mild gambier shows a smooth adsorption curve, astringent quebracho acts in a strikingly different manner, giving greater fixation of tannin and showing a sharp maximum followed by an abrupt decline. A very decided difference in the action of typically mild and astringent extracts is manifested and the value of further study to establish the reasons therefor is quite apparent.

TWO commonly used vegetable tans, gambier and quebracho, were selected for examination: gambier on account of its mild action and quebracho on account of its very astringent nature. The fixation of the tannins of these substances through a range of concentration up to saturated solutions and for the intervals of 6 hrs., 72 hrs., and 2 wks. has been measured.

GENERAL METHOD

Portions of hide powder equal to 10 g. of the absolutely dry material were placed in 400-cc. rubber-stoppered bottles. Six different concentrations of tan solution were poured on the hide powder specimens and the bottles rotated in a tumbling machine for the desired times, at the ends of which the contents were filtered through muslin bags. The filtrates were saved for gelatin-salt test and the tanned hide powder was washed with running water and transferred back to the bottle, covered with 300 cc. of water, tumbled for 0.5 hr., and filtered again. This washing operation was repeated until the filtrate no longer showed a dark color upon addition of a few drops of ferric chloride solution.

When the filtrate showed no nontannins present, by means of the ferric chloride test, the washed tanned powder was squeezed out, dried on flat dishes in a current of warm air, and bottled to await analysis.

The analysis consisted in the determination of moisture, protein (N × 5.614), fat (matter extracted by chloroform), and ash. The sum of the percentages of these constituents subtracted from 100 gave the per cent of tannin according to the definition of Wilson and Kern,[4] that tannin is that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. The resistance of the protein-tannin compound to washing has been demonstrated by the same authors.[5]

DELICACY OF FERRIC CHLORIDE TEST

The writers considered all nontannin removed when 25 cc. of the washings gave no appreciable change of color upon addition of 3 drops of molar ferric chloride solution. The delicacy of this test as applied to solutions of gallic acid and pyrogallol is shown below.

1 Part in	COLOR
	Gallic Acid
1,000	Greenish black
10,000	Dark greenish yellow
50,000	Greenish yellow
75,000	Faint greenish
100,000	Yellow, as obtained with water
	Pyrogallol
1,000	Dark brown
20,000	Brown
50,000	Slight brown tint
75,000	Slightly brownish yellow
100,000	Very slight deepening of yellow color of blank

It is evident that this ferric chloride test is delicate to 1 part in 75,000. Consequently there was not more than this amount of nontannin present in the last washings of the tanned powders, if gallic acid and pyrogallol are considered typical examples of nontannins.

TESTS ON GAMBIER

SIX-HOUR ADSORPTION—From a gambier paste containing 39.2 per cent of total solids (as determined by A. L. C. A. method), a stock solution was prepared by dissolving 1000 g. in water at 85° C., cooling, and adjusting approximately to 2 liters. It was filtered through cheesecloth to remove coarse debris. From this stock solution the various dilutions were prepared.

SOLUTION	Approximate Concentration Grams Moist Gambier per Liter	Total Solids Grams per Liter (Exact)
1	25	9.8
2	60	23.5
3	100	39.2
4	200	78.4
5	350	137.2
6	500	196.0

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[1] Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Contribution No. 384 from the Chemical Laboratories of Columbia University.

[3] Assistant Professor.

[4] THIS JOURNAL, **12** (1920), 465.

[5] *Ibid.*, **12** (1920), 1149.

Volumes of 200 cc. each of the above solutions were placed on portions of 1920 hide powder, equal to 10 g. of absolutely dry powder and rotated at room temperature for 6 hrs.

Filtrate No.	Gelatin-Salt Test	No. of Washings
1	—	9
2	Practically —	12
3	+	30
4	+	61
5	+	41
6	+	41

In the column headed "No. of Washings" are indicated the number of times the samples were washed to get a negative ferric chloride test. Under the heading "Gelatin-Salt Test," it is seen that all the tannin present in solutions No. 1 and No. 2 was removed by the hide powder.

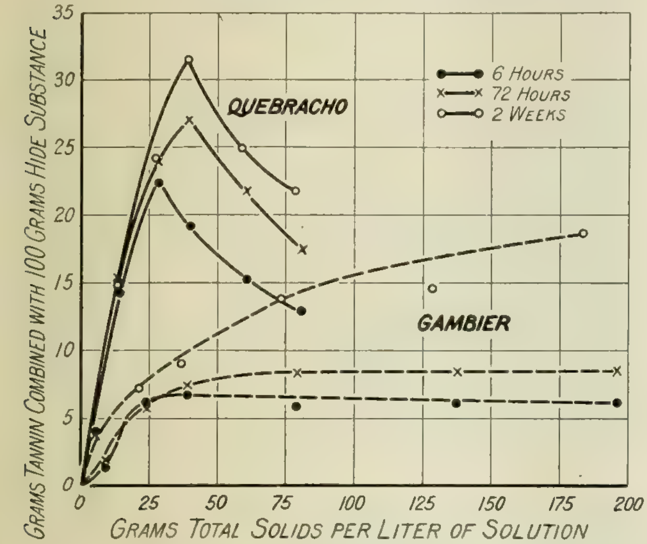

Fig. 1

The analytical data are given in Table I and plotted in Fig. 1.

Table I—Composition after 6-Hr. Adsorption

Sample	1	2	3	4	5	6
Per cent water	14.37	13.86	10.75	15.33	14.25	14.04
Fat	0.65	0.72	0.57	0.40	0.80	0.67
Ash	0.16	0.15	0.22	0.30	0.21	0.26
Protein	83.66	80.30	83.01	79.33	79.76	80.06
Tannin (by diff.)	1.16	4.97	5.45	4.64	4.98	4.97
G. tannin per 100 g. protein	1.39	6.19	6.57	5.85	6.24	6.21

seventy-two-hour adsorption—The filtrates from Samples 1 and 2 gave a negative gelatin-salt test, showing that all the tannin had been removed from solution by the hide protein. Filtrate 3 gave a slightly positive test, while all the rest were strongly positive. The number of washings required to remove all nontannins from the hide powders were: No. 1, 18; No. 2, 35; No. 3, 60; Nos. 4, 5, and 6, 66. Table II records the analytical data obtained.

Table II—Composition after 72-Hr. Adsorption

Sample	1	2	3	4	5	6
Per cent water	9.70	11.16	12.01	10.65	10.48	10.20
Fat	0.71	0.68	0.47	0.38	0.43	0.30
Ash	0.22	0.21	0.24	0.29	0.24	0.27
Protein	87.61	83.17	81.29	81.92	81.97	82.24
Tannin (by diff.)	1.76	4.78	5.99	6.76	6.88	6.99
G. tannin per 100 g. protein	2.01	5.75	7.37	8.25	8.39	8.50

two-week adsorption—New solutions of gambier were prepared as nearly as possible like the first described, and 1921 instead of 1920 hide powder was used.

The definition that formation of leather is the conversion of hide substance to an insoluble imputrescible substance is illustrated here. In Solutions 3 to 6, where an excess of tannin is shown by the gelatin-salt test, there was no decomposition as in the case of 1 and 2, where there was not sufficient tannin present to form the insoluble, imputrescible, protein-tannin chemical compound.

Solution	Approximate Concentration Grams Moist Gambier per Liter	Total Solids Grams per Liter (Exact)	Filtrate Gelatin-Salt Test	Filtrate No. of Washings
1	25	9.15	—	..[1]
2	60	21.96	—	11[2]
3	100	36.6	Slight +	43
4	200	73.2	+	53
5	350	128.1	+	53
6	500	183.0	+	53

[1] Badly decomposed and hence discarded.

[2] Slight decomposition.

Analytical data for this series of experiments are recorded in Table III.

Table III—Composition after 2-Wk. Adsorption

Sample	2	3	4	5	6
Per cent water	18.84	16.28	17.16	16.37	16.45
Fat	0.25	0.15	0.30	0.20	0.18
Ash	0.24	0.60	0.66	0.53	0.59
Protein	75.31	76.09	71.93	72.32	69.71
Tannin (by diff.)	5.36	6.88	9.95	10.58	13.07
G. tannin per 100 g. protein	7.12	9.04	13.83	14.63	18.75

Tests on Quebracho

six-hour adsorption—A stock solution was prepared by dissolving 150 g. of dry quebracho extract at 85° C., cooling, and making up to about 1500 cc. with distilled water. The total solid content of the dry extract was 80.5 per cent. Six solutions were made as noted below, and weights of hide powder equal to 10 g. absolutely dry substance plus 200 cc. of the solutions were placed in bottles and rotated, etc., as previously described.

Solution	Approximate Concentration Grams Quebracho per Liter	Total Solids Grams per Liter (Exact)	Filtrate Gelatin-Salt Test	Filtrate No. of Washings
1	6.3	5.07	—	11
2	17.0	13.7	—	11
3	35.0	28.1	+	44
4	50.0	40.2	+	44
5	75.0	60.3	+	44
6	100.0	80.4	+	44

It should be noted that Solutions 1 and 2 were completely detannized. The analytical results are listed in Table IV.

Table IV—Composition after 6-Hr. Adsorption

Sample	1	2	3	4	5	6
Per cent water	15.53	15.78	14.99	15.09	15.54	15.67
Fat	0.51	0.63	0.39	0.32	0.31	0.26
Ash	0.22	0.25	0.29	0.24	0.25	0.25
Protein	80.50	72.88	68.92	70.84	72.86	75.12
Tannin (by diff.)	3.24	10.46	15.41	13.51	11.04	9.70
G. tannin per 100 g. protein	4.03	14.35	22.36	19.07	15.15	12.91

A notable difference in the amount of tannin combined with the collagen at different concentrations of liquors is shown by this, and the 72-hr. and 2-wk. adsorptions. Inspection of Fig. 1 brings this out very strikingly.

seventy-two-hour adsorption—The liquors were identical with those used in the 6-hr. experiment.

Filtrate	Gelatin-Salt Test	No. of Washings
1	—	18
2	—	18
3	Slightly +	60
4	+	60
5	+	60
6	+	60

Solutions 1 and 2 were completely detannized, whereas Solution 3 showed but a trace of tannin left, in contradistinction to the 6-hr. experiment where a definite excess of tannin in the filtrate was noted. Table V contains the analytical data.

Table V—Composition after 72-Hr. Adsorption

Sample	1	2	3	4	5	6
Per cent water	17.73	16.60	12.52	12.22	12.13	12.63
Fat	0.47	0.62	0.65	0.53	0.49	0.46
Ash	0.22	0.22	0.35	0.25	0.23	0.25
Protein	78.49	71.53	69.77	68.52	71.58	73.74
Tannin (by diff.)	3.09	11.03	16.71	18.48	15.57	12.92
G. tannin per 100 g. protein	3.94	15.42	23.95	26.97	21.75	17.52

TWO-WEEK ADSORPTION—The solutions of quebracho were made up as nearly as possible like those in the 6- and 72-hr. experiments. The total solid contents, number of washings of the tanned hide powders, etc., were as follows:

SOLUTION	Approximate Concentration Grams Quebracho per Liter	Total Solids Grams per Liter	FILTRATE Gelatin-Salt Test	FILTRATE No. of Washings
1	6.3	4.9	−	..[1]
2	17	13.3	−	11
3	35	27.3	Lost	42
4	50	39.0	+	42
5	75	58.5	+	42
6	100	78.0	+	42

[1] Decomposed and hence discarded.

TABLE VI—COMPOSITION AFTER 2-WK. ADSORPTION

SAMPLE	2	3	4	5	6
Per cent water	17.85	15.23	14.68	15.06	15.38
Fat	0.23	0.14	0.23	0.24	0.21
Ash	0.29	0.39	0.36	0.43	0.40
Protein	71.03	67.82	64.44	67.52	69.01
Tannin (by diff.)	10.60	16.42	20.29	16.75	15.00
G. tannin per 100 g. protein	14.92	24.21	31.49	24.81	21.74

The courses of the curves obtained by plotting the grams of tannin combined with hide substance against the concentration of the tan liquors are shown in Fig. 1.

COMPARISON OF GAMBIER AND QUEBRACHO

The action of these two vegetable tanning extracts is striking. As would be expected in an orthodox adsorption, the gambier curves are approximately parabolic, while the sharp maximum shown by quebracho at concentrations between 30 and 40 g. total solids per liter is exceedingly interesting. The writers believe that in neither case is it a question of a simple physical adsorption. It is chemical combination, as pointed out in one of our reports on chrome tanning.[6]

An explanation for the great difference in behavior between the two extracts is not forthcoming at this time. In the case of chrome tanning, evidence for definite chemical compounds has been offered; this is not possible here on account of the very complex chemical nature of the vegetable extracts. The answer may be reached by study of the action of pure tannin under various conditions.

The mild action of gambier as contrasted with the very astringent nature of quebracho is graphically shown by the steep rise of the quebracho curves with the points distributed on smooth curves, while the points on the 6-hr. gambier curve are rather ragged.

The reactions of the solutions do not seem to be the cause of the sharp breaks and declines in the quebracho curves, for while no measurements were made of the H-ion concentrations in the experiments here reported, a series of values obtained in preliminary 6-hr. adsorption experiments did not show any variations great enough to be of any significance in the point at issue.

GAMBIER

G. total solids per liter	3.9	9.8	19.5	39.0	97.5	195.0
Log C_{H^+} before adsorption	−5.25	−5.16	−5.11	−5.08	−5.04	−5.00
Log C_{H^+} after adsorption	−5.71	−5.43	−5.37	−5.29	−5.12	−5.04

QUEBRACHO

G. total solids per liter	2.5	4.9	9.8	19.5	39.0	78.0
Log C_{H^+} before adsorption	−5.07	−5.00	−4.97	−4.91	−4.84	−4.79
Log C_{H^+} after adsorption	−5.60	−5.46	−5.35	−5.28	−5.28	−5.04

The only difference between the reactions of the two sets of solutions is a slightly greater acidity in the case of quebracho, but since the isoelectric point of hide protein is at 10^{-5} (unpublished result obtained in this laboratory), the H-ion concentrations of the stronger quebracho solutions would render the hide more electropositive than the weaker liquors; hence, according to the theory of Wilson,[7] the negative tannin should combine with the hide more readily. Further experiments with varying H-ion concentrations are necessary to settle this point.

Since quebracho is very astringent, *i. e.*, of low nontannin content, the abrupt drop at 30 to 40 g. concentration would indicate that the surfaces of the hide powder particles are so heavily tanned that they are rendered impermeable to tannin and hence the interiors of the particles are unaffected, thus accounting for the smaller amount of tannin fixed by the hide in the strong solutions.

It is well known that gambier, on the other hand, contains a larger amount of nontannins than quebracho. In terms of conductivity measurements made in this laboratory, it is much richer in electrolytes. The result is that the nontannins, being of lower molecular weight, diffuse more readily into the hide substance than does tannin, and undoubtedly combine chemically with the hide protein, although not so firmly as tannin. As pointed out by Wilson,[8] tannin that would otherwise have combined with the outer surface is thus enabled to penetrate into the interior, and accomplishes combination with the hide through displacement of the nontannin hide compound, since it forms a protein compound of much lower solubility. The result is a slower reaction, but one which takes place uniformly throughout the hide substance, thus giving the lower smooth curve for gambier as contrasted to the rapid rise, with abrupt decline, obtained with quebracho.

ACKNOWLEDGMENT

We take pleasure in expressing our indebtedness to Messrs. A. F. Gallun and Sons Company, of Milwaukee, for their generous support of this investigation.

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[6] THIS JOURNAL, **13** (1921), 31.

[7] *J. Am. Leather Chem. Assoc.*, **12** (1917), 108; **14** (1919), 450

[8] *J. Am. Leather Chem. Assoc.*, **15** (1920), 374.

"Baking Technology"

In our March editorials we sketched the part which chemistry and research have played in one baking industry. As another step along the same line, we are glad to note the appearance of *Baking Technology*, a monthly publication of the American Bakers' Association.

To quote from the editorial page of the first number:

> As the official journal of the American Bakers' Association, *Baking Technology* will keep member bakers informed of the progress of association activities. It will tell the story of scientific achievements in the laboratories of the Institute [of Baking]. It will summarize the results of work in the technical and service laboratories, that the data there obtained may be available for all. It will serve as the link between the school and the industry, outlining the courses, developing the contacts between bakers and students, reporting results as they promise to be of value. It will officially proclaim the standard set by the Institute for flour, sugars, shortenings, and all other materials used in the bakery. It will carry the official methods worked out for the testing of these materials.

An interesting feature of the publication is a double page of short editorials and bread stories, written in a form suitable for use in newspaper columns. This has the same purpose as the clip sheet which the A. C. S. News Service issues, of giving the public correct information rather than the inaccurate statements which so often appear in the newspapers.

Atomic Weights and Isotopes

On March 6 to 10, 1922, F. W. Aston, M.A., D.Sc., F.R.S., Fellow of Trinity College, Cambridge, England, gave a series of five lectures before the Franklin Institute, Philadelphia, Pa. The subjects of the lectures were "The Atomic Nature of Matter," "Discharge of Electricity in Gases," "Positive Rays and Their Analysis," "The Mass-spectograph," and "Isotopes and the Structure of the Atom."

Dr. Aston is also to lecture before several universities and other organizations during his stay in this country.

Preparation and Evaluation of a Decolorizing Char from Bagasse[1]

By C. E. Coates[2]

Louisiana State University, Baton Rouge, Louisiana

There is need of a more accurate method of evaluation of decolorizing chars. In the present work, a commercial char of high efficiency was selected empirically as a standard and used in measuring the relative efficiency of a series of experimental chars made from bagasse. By comparing the filtrates obtained from the standard char and the experimental chars, a more accurate comparison can be made than is possible between the dark initial solution and its decolorized product. The experiments demonstrate the importance of uniform acidity in comparing decolorizing power.

Bagasse char, heated without treatment to 900°, had a decolorizing power of 66 (standard = 100), which was increased to 86 by boiling with sodium hydroxide, and to 170 by subsequent boiling with hydrochloric acid. Chars prepared by this method had a decolorizing power of from two to two and a half times that of the standard char. In addition to removing organic coloring matter, the chars showed a marked power of absorbing iron salts. Yellow commercial hydrochloric acid, which was used in washing the char, came through absolutely colorless. This suggests a possible technical application of highly activated chars in the removal of iron from commercial hydrochloric acid.

During the last six years a great deal of work has been done on activated chars, stimulated no doubt by their very great importance in gas warfare. It has become evident that for some reason there is little relationship between the gas absorbing power and the color adsorbing power of chars, though no satisfactory explanation of this lack of relationship has yet appeared. It is perhaps too soon, therefore, to do more than add a few facts to those already at our disposal, in the hope that we may soon be able to reach a point where we can generalize rationally and not be driven to empirical conclusions.

In 1914 William Clacher[3] published an account of work on some bagasse chars, with the idea that the results might be applied technically. The process outlined by Clacher differs from one mentioned by Weinrich a number of years ago in certain patent specifications, in that Weinrich used the charred bagasse without subsequent chemical treatment, mainly as a filter aid, while Clacher activated his char by boiling with strong caustic soda, for the purpose of removing the siliceous ash, followed by washing with acid. So far as the present writer knows, neither process has ever been carried out technically.

Dilute sodium hydroxide has been used for many years to revivify spent bone chars. The purpose of the sodium hydroxide is to change the conditions of adsorption at the free surface of the carbon so that adsorbed substances may pass again into solution, and to dissolve certain alkali-soluble compounds. These substances include coloring matters, gums, colloids of one type or another, and mineral salts. In revivifying boneblack, the soda process was usually considered more expensive than burning.

The use of stronger solutions of soda to activate inactive wood chars seems to the writer a different thing in many ways from its use in revivifying spent bone chars. It would naturally occur to any chemist, who had to deal with a char with a siliceous skeleton, to extract this silica. Boneblack can be made much more active by extracting it with hydrochloric acid, thus removing the insoluble tricalcium phosphate, increasing the porosity, and leaving a greater amount of free carbon surface available for adsorption. This is an ordinary laboratory procedure. In a similar way a siliceous char boiled with sodium hydroxide would lose its silica in the form of soluble sodium silicate, becoming more porous and more active. This procedure, however, would be without purpose in the case of bone char, which has a calcium phosphate base, and was probably not tried out on wood chars until the latter were developed into decolorizing chars some twelve to fifteen years ago. When high power chars of vegetable origin were developed from wood giving an ash of low silica content, the supporting skeleton was supplied by impregnating with lime or some other mineral substance, which was subsequently extracted by hydrochloric acid. Chars made of vegetable material high in silica, on the other hand, were extracted with sodium hydroxide, with the same general purpose in view.

The growing importance of vegetable chars, which was stimulated by the successful work of Sauer and Wijnberg, has caused a good many chemists to seek different sources of decolorizing chars during the last few years. Bagasse, being a by-product of the cane-sugar industry, has naturally received considerable attention, and a number of experiments have been made with it by numerous workers, including the writer. The reports of these experiments vary considerably. It has therefore been thought best to repeat them for the purpose of ascertaining, if possible, the cause of these differences. In order to rule out the personal equation three lots of bagasse were treated separately by different men, first by the writer, then under his direction by Mr. A. D. Lipscomb and by Mr. P. M. Horton. The results in all cases were practically identical.

It soon became evident that in most published accounts of the evaluation of chars the conditions of the tests were rarely stated with any detail and definiteness, nor was any one method used generally, nor were the results expressed in the same mathematical terms. It was determined, therefore, to test the effect upon the results of slight changes in conditions and to establish a standard method for work, which, while not altogether satisfactory, would at least have the merit of being definite.

CALCULATION OF RESULTS

In sugar work, decolorizing chars are probably of value in accordance with the amount of color they leave in the solution, rather than the amount which they take out. The usual Stammer and Duboscq figures give us roughly the percentage of color removal. On this basis a carbon which would remove 45 per cent would be one-half as good as a carbon which would remove 90 per cent total color, a statement which is incorrect technically. Similarly, a carbon which would remove 90 per cent of color would be called almost as good as one which would remove 95 per cent of color. This statement is also incorrect. On the other hand, it is, of course, not quite correct to call one which leaves 5 per cent twice as good as the one which leaves 10 per cent. None the less, it is the writer's opinion that the second is the less inaccurate method of the two, and it was adopted for his work. These points were raised by Zerban some time since. The writer agrees with his point of view, in the main; but undoubtedly we need a more accurate system of evaluation. In order to get a rough idea as to the initial intensity of color, the sugar solutions were read against a Stammer double plate. While the tint of the solution generally differed materially from that of the plate, it was none the less found possible to get scale readings which were surprisingly uniform. The same solutions were then read before and after decolorizing, in the Duboscq colorimeter, and the comparison was made directly between the lengths of columns having the same tint, no allowance being made for the fact that, mathematically, color removal is not quite proportionate to length of column. The solutions were also read with a Hess-Ives tint photometer.

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[1] Presented before the Division of Sugar Chemistry and Technology at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Dean, Audubon Sugar School.

[3] *Intern. Sugar J.*, **1914**, 64.

For the sake of comparison, a good grade of commercial decolorizing char of high efficiency was taken as a standard, and its decolorizing power was called 100. This standard is, of course, purely empirical, and might be omitted if desired, but it was found to be a convenient way of testing the relative decolorizing power of a series of experimental chars. Moreover, by comparing the filtrates obtained under standard conditions from the standard char and the experimental char, respectively, it was found that a more accurate comparison could be made between the light filtrates than between the dark initial solution and its decolorized product. Table I illustrates these points.

TABLE I

(Stammer reading on original solution, 3.5)

	Duboscq Colorimeter		
	Equivalent Lengths of Column Mm.	Color Removed	Color Left
Filtrate from standard char	100	83	17
Initial solution before decolorizing	17	..	..
Filtrate from experimental char	100	92	8
Initial solution before decolorizing	8	..	..
Filtrate from standard char	47	..	..
Filtrate from experimental char	100	..	..

Efficiency experimental char relative to standard $\frac{17}{8} = 213$

Efficiency experimental char relative to standard $\frac{100}{47} = 213$

It will be noticed that by direct comparison of the standard char filtrate with the experimental char filtrate the same figures are obtained as by the indirect comparison with the molasses solution. As the tints of the filtered solutions are more easily matched, this method was used in calculating the following data. (See also Tables II, III, and V.)

TEST SOLUTION

As a standard test solution to be decolorized, a 3 per cent solution of blackstrap or third molasses was chosen, because a solution of this type had been used by Zerban and others in char work. Different samples of molasses were found to differ materially in their color content, but the comparative figures on decolorizing were practically the same on all molasses samples employed. For this reason it may be inferred that the general nature of the coloring matters in third molasses is practically the same, and hence it may safely be used in obtaining comparative figures. It may be noted, however, that it is not possible to compare results obtained on molasses with those obtained on other types of colored organic material, as, for instance, crude glycerol. The stock molasses solution was boiled and filtered with kieselguhr with practically no loss in color. Inasmuch as fermentation brought about color changes a fresh solution was made up every 2 days.

METHOD OF WORK

To 200 cc. of the solution in a 500-cc. flask, 6 g. of char were added, the contents brought to a boil, then stoppered and heated in a boiling water bath for 10 min. with occasional agitation. The flask was then cooled and the contents filtered, discarding the first few cc. which were usually cloudy. In several experiments the flasks were boiled 5, 15, and 20 min. There was hardly an appreciable difference in the decolorizing effect after 5 min. and none at all after 10 min.; the latter was taken as the standard time for boiling. The filtrates should be read after they are thoroughly cold. Though there is little difference in color in the same filtrate at 20° and 30°, it generally becomes lighter as the temperature rises. This phenomenon is particularly noticeable with sirups, but different sugar solutions show it to different degrees.

ACIDITY

The importance of uniform acidity in comparing decolorizing power cannot be overestimated, as will be seen from Table II, recording the results of tests made with definite degrees of acidity. Acidities were obtained with phosphoric acid and alkalinities with sodium hydroxide, with phenolphthalein as an indicator. pH values were obtained on a different series of solutions.

TABLE II

3 per cent molasses solution, made acid with phosphoric acid and alkali with NaOH

Acidity *N*	Color before Decolorizing	Apparent Efficiency Standard Char
0.03	Light yellow	200
0.015	Light yellow	150
0.007	Brownish yellow	100
0.0035	Dark yellow-brown	99
0.0015	Dark reddish brown	80
0.007	Lighter, but redder	75
Alkalinity, *N* 0.07	Still lighter, but red	60

In this case 200 cc. of the molasses solution were brought to the acidities indicated and decolorized with 6 g. of char. The acidulated solutions were not of comparable colors because of the difference in tint, but there was no difficulty in obtaining comparable readings after decolorizing. It will be noted that by simply changing the acidulation there was an apparent increase in efficiency of the char of 100 per cent and a corresponding decrease when the solutions were made alkaline. The figures were calculated on color remaining in solution. From the foregoing one might reasonably conclude that comparisons of decolorizing chars where no mention is made of acidities are of somewhat doubtful value. It might be added that although these apparent decolorizing effects are only apparent, there seems nevertheless to be a certain relationship in actual color removed, as the filtered solutions when brought to the same acidity retained the same order of decolorization, though not to the same extent.

The following colorimetric readings at varying acidities on a molasses solution of different origins were made at our request by Mr. W. G. Raines, Jr., with the Hess-Ives tint

TABLE III

Solutions Used Acidity, *N*	Red	Green	Blue	Total	Total Color Remaining
0.02	46	76	85	207	49.5
	50	77	84	211	53
0.015	50	78	85	213	55
	48	77	84.5	209.5	51.5
0.01	55	80	85	220	61
	52.5	79	85	216.5	58
0.005	65	83	85	233	79.5
	69	83	85	238	79.5
0.003	69	83.5	85.5	238	81.5
	71	83.5	85	239.5	83
Neutral	71	84	85.5	240.5	86
	71	84	85	240	85
Alkalinity, *N*					
0.003	64	84	85.5	233.5	76
0.005	61	84	85.5	230.5	72.5
	62	83.5	85	230.5	72.5
0.01	52	83	84.5	219.5	60.5
0.02	50	82	84	216	57

photometer. The chart used in the color determinations is that published by Zerban.[4] The readings are in duplicate series. It will be noted that there was no great difference in the amount of blue remaining, that the green was apparently removed to a slightly greater extent in acid solutions, and that the red was apparently much more affected.

In the following tests the acidity of the solutions to be decolorized was kept at a constant acidity of 0.007 *N*. This is not far from the optimum clear juice acidity in raw sugar making, which in good practice ranges from 0.004 to 0.007. In melting raw sugars the optimum acidity for first liquors seems to be from 0.0015 *N* to 0.0025 *N*. In the direct manufacture of plantation granulated the best clear juice acidities, as determined by experience, range from 0.009 *N* to 0.011 *N*.

PREPARATION OF CHARS

About 8 lbs. of bagasse were charred in each of three series of experiments. The bagasse was heated in a large iron sand bath, which was heated red hot by a battery of Méker burners and covered with a similar sand bath, the two being separated by a heavy triangle of iron wire and thus held about one-eight inch apart. This gave a fairly satisfactory retort, from which gases could escape readily without any increase in pressure. At the end of 15 or 20 min. most of the volatile matter had been driven off and the char rendered so brittle that one could powder it for subsequent treatment. The temperature of the retort ranged from 500° to 600° C., as recorded by a Northrup pyrometer. The percentage of recovery was about 50 per cent on the basis of dry matter. The char still contained a large quantity of substances volatile at higher temperature, as was evidenced by the fact that when heated to 800° it gave off gas with such rapidity as to blow the char in part from the clay crucible if the temperature were raised too rapidly. The char was ground to 70 to 90 mesh, and called primary Char A, and used in the subsequent preparation of activated chars with the electric furnace. Charring in two stages was found more convenient than charring in one stage on account of the bulky nature of the raw material. The results obtained in the two cases were identical.

SIZE OF CHAR GRAINS

The chars were cooled, ground, and sifted, and separate tests were made of the various sieve fractions. Chars between 70 and 90 mesh were the most effective, and did not differ appreciably in decolorizing power. These portions, therefore, were selected for the experiments. A small quantity of char of 100 mesh upward was also obtained. This was tested separately and showed about the same qualities as a 70 to 90 char, to which it was subsequently added. The high mesh chars gave somewhat slower filtration, with no appreciable increase in decolorizing power.

PRELIMINARY EXPERIMENTS

SOLUTIONS—A solution containing 400 g. of granulated sugar and 200 g. of first molasses was diluted to 2000 cc. This gave Solution 1, of 27.8 Brix and a reading against the Stammer double plate of 3.5. It approached in color and composition a rather dark sirup in ordinary sugarhouse practice. To 160 cc. of this solution (containing 50 g. of total solids) in a 250-cc. flask were added 5 g. of char, or 10 per cent on total solids. The stoppered flask was heated to 95° to 100° C. for 10 min., filtered, and cooled. Color comparisons were made on a Duboscq type colorimeter. Four solutions corresponding to Solution 1 were made up from different samples of molasses; 2, blackstrap; 3, blackstrap; 4, high-grade first molasses. In all cases the solutions were acidulated to 0.007 *N*, with phosphoric acid.

CHARS—Bagasse chars were made as follows:

CHAR B—By heating Char A to 600° with a battery of Méker burners, washing water-soluble ash out with hot water, and drying.

CHAR C—By heating B to 800° in an electric furnace for 1 hr.

CHAR D—By boiling C for 10 min. with 15 per cent sodium hydroxide on weight of char plus enough water to make a cream, the final percentage being about 4 per cent sodium hydroxide solution.

CHAR E—Boiling D 5 min. with 1:1 hydrochloric acid.

In Table IV the Stammer reading gives the approximate color, and the decolorizing powers are given in terms of standard char = 100.

TABLE IV

SOLUTION	Stammer Reading	Decolorizing Power of Chars B	C	D	E	Standard
1	3.5	25	..	..	102	100
2	2	..	32	..	110	100
3	1.5	..	36	91	133	100
4	6	..	..	83	120	100

This bagasse char was not as active as batches subsequently made, probably because the sodium hydroxide solution was too weak. Tests made using the same amounts of molasses and omitting the sucrose gave similar results. The results show that:

1—The presence of sucrose did not materially affect the decolorizing power.

2—Bagasse char, when properly made, has a distinct decolorizing power before it is treated with sodium hydroxide (Columns B and C).

3—This decolorizing power is greatly increased by boiling with sodium hydroxide (Column D).

4—It is still further increased by boiling the char extracted with sodium hydroxide with a 1:1 solution of hydrochloric acid (Column E).

FURTHER EXPERIMENTS ON BAGASSE CHARS

The work was repeated with more attention to detail, it having become evident that the quality of the char was materially affected by several slight changes in process. For instance 20 g. of Char C were treated with 3 g. of sodium hydroxide, or 15 per cent by weight. To this was added enough water to enable the solution to boil readily. At the end of 15 mins.' boiling the ash content had not been greatly reduced. A rough estimate showed that about 100 cc. of water had been added, giving a 3 per cent solution of sodium hydroxide, which attacked the silica slowly. If, however, this solution was allowed to boil down to a thick porridge, thus increasing the concentration of the sodium hydroxide solution, the silica content was reduced and the activity of the char materially increased. It was also noted that for different samples of molasses a given char showed different percentages of color removed compared with the standard, and the ratios of color removed by different chars on these different molasses samples were not constant.

CHAR A—Ash, 11 per cent; SiO_2, 7.05 per cent; decolorizing power, 0.0.

CHAR F—This was made by boiling Char A with sodium hydroxide, 20 per cent on weight of char, for 15 min., washing with water, then with dilute acid, and drying. Ash, 3.3 per cent; SiO_2, 0.9 per cent; decolorizing power, 50.

CHAR G—Inasmuch as chars made at higher temperatures had shown more decolorizing power, Char A was boiled with sodium hydroxide as for Char F and then heated to 850° C. for 1 hr. A quantity of gas was given off during this stage. Ash of Char G, 8 per cent; SiO_2, 3.2 per cent; decolorizing power, 225.

CHAR H—From the foregoing it was evident that the temperature of charring was of prime importance. Char A, therefore, was heated without treatment with sodium hydroxide to 900° for 2 hrs., giving Char H, with a decolorizing power of 66.

CHAR I—Char I was prepared by boiling Char H 30 min. with 20 per cent weight of char of sodium hydroxide, which gave a decolorizing power equal to 86.

CHAR J—Char I was boiled with hydrochloric acid, and the resulting Char J showed a decolorizing power of 170.

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[4] *Louisiana Planter*, **1918**.

From the foregoing it is evident that bagasse char heated without treatment to 900° had a decolorizing power of 66, which was increased to 86 by boiling with sodium hydroxide, and to 170 by subsequent boiling with hydrochloric acid. Owing to the initial high temperature employed in charring, less ash or SiO_2 was removed by the soda under the conditions mentioned above than in the previous tests.

Approved Method of Preparation

As a result of these experiments, Char K was prepared as follows: Char A was heated 1 hr. to 800° to 850° C., boiled for 2 hrs. with a 20 per cent sodium hydroxide solution, with the addition of water from time to time to keep the concentration practically constant, washed, boiled with 1:1 hydrochloric acid, washed, and dried by heating to about 200°. The residual Char K was compared with several commercial chars of good quality with the following results:

	Char K	Norit	Darco	Standard
Decolorizing power..........	260	102	110	100
Apparent specific gravity.....	0.136	0.241	0.343	...

Several batches of Char K were made, all having from two to two and one-half times the decolorizing power of the standard char. These batches seemed to have about the same physical properties, but differed in ash content. In addition to removing organic coloring matter from solutions, Char K showed a marked power of absorbing iron salts as well. The acid used in washing was yellow, commercial hydrochloric acid, but the filtrate came through absolutely colorless, which might indicate that commercial hydrochloric acid could be freed of iron technically by the use of high-power activated chars. This problem is now being investigated in this laboratory. In the preparation of Char K it was noted that if the temperature were raised to much over 900° there was a loss in decolorizing power; that the 20 per cent solution of sodium hydroxide in 1 hr. gave practically as efficient a char as in 2 hrs., and that it was almost impossible to remove either all the alkali or all the acid by any ordinary amount of washing. Of the two, the acid was the more difficult to wash out. The writer attributes this to the fact that the acid entered the pores of the char and thus escaped the wash water. With this in mind, the washed char was again raised to from 200° to 300° C., or below the kindling point, in a current of air, in order to volatilize any hydrochloric acid which might still be in the char. The resulting char after a 10-min. boiling with water gave a solution which was practically neutral. Technically, this is a matter of some consequence, as a number of commercial chars which were tested for acidity proved to be sufficiently acid to interfere materially with the refinery process. In one case a noticeable amount of inversion was traced to this source. Although there is no absolute proof thereof, the writer is inclined to attribute the harmful effect of extremely high temperatures to the partial graphitizing of the carbon, graphitic carbon having very little decolorizing power. High temperature would also cause incipient fusion of any silicates still present, which would spread as a protecting film over the adjacent free carbon surface. These silicates and free silica are attacked and rendered soluble by a boiling solution of 20 per cent sodium hydroxide, this action being slowest when the silicate and silica have been subjected to very high temperatures. The removal of the silicate film and of silica itself would expose a greater surface of free carbon and increase decolorizing power. Certain films formed by organic materials of unknown nature are also removed by the sodium hydroxide. Some films of inorganic origin, such as those formed by calcium hydroxide, iron oxide, and the like, left by the action of soda on the ash, are removed by the hydrochloric acid treatment with the formation of soluble chloride. Possibly some acid-soluble organic films are also removed, but of this the writer found no direct proof.

Char K was very low in apparent specific gravity, and was the best filter aid of any char tested. It was revivified by boiling first with 5 per cent sodium hydroxide and then with 5 per cent hydrochloric acid with excellent results. It was also revivified by retorting in the usual way with even better results.

Comparison with Boneblack

Since reference is frequently made to boneblack decolorization, standard fresh boneblack, obtained from a boneblack refinery, was sifted and the 20–35 mesh fraction was used for tests. Under the conditions outlined above, 6 g. per 200 cc. gave no appreciable decolorization. If the boneblack was boiled with hydrochloric acid, filtered, and heated to dull red heat, it gave 20 per cent decolorization, as compared with standard.

Tint Photometer Readings

Inasmuch as the readings on the Hess-Ives tint photometer are frequently taken as a basis of comparison a series of tests (Table V) were made with this instrument. A 3 per cent blackstrap solution was used with 3 g. of char per 100 cc., the acidity was 0.007 N, the heating was carried out as previously described, and 70 cc. of the filtrates were placed in the cells for reading.

Table V

	Red	Green	Blue	Total Color Left
Standard molasses solution, untreated.	72	87	90	102
Same with 3 g. boneblack	69	87	90	100
With 3 g. commercial Char X	30	61	83	34
With 3 g. standard char...............	13	35	56	14
With 3 g. Char J......................	7	22	49	9.5
With 3 g. Char K......................	2	12	35	5.5

It will be noticed that the bagasse char is particularly efficient in removing the red, which from a technical standpoint is probably the most important color to remove. Comparing 14, the color left by the standard, with 5.5, the color left by Char G, we obtain 255. A similar comparison by means of the Duboscq colorimeter has given 260, which would indicate that color determinations made with either instrument give figures which are practically identical from a technical standpoint.

These experiments on bagasse char have been described with considerable detail, because certain other articles on this subject have been so lacking in detail that it has been difficult to interpret the results. It might not be amiss at this point to call attention to another factor in comparing the value of decolorizing chars. If 3 g. of char, having been used once, are sucked dry without washing and used again on a second 100 cc., considerable color will be removed. This can be repeated a number of times before all decolorizing power is lost. There would seem to be an equilibrium reached between the concentrated film of color on the surface of the char and the dispersed color in the liquid. Just what this equilibrum is, it is difficult to say. The problem is now under investigation by the writer and Mr. P. M. Horton, who hope to have results ready for publication in the near future.

Degrees for Sale in American Universities

For the benefit of our foreign members and readers, we wish to say that no reputable institution in America makes a practice of selling academic degrees. One institution in the District of Columbia which may have made such offers in foreign publications has no standing, no laboratories, and no equipment for university work. It may be added that this particular activity has had the attention of various government investigators, but since it is difficult to prove actual fraud in a matter of this kind, especially since its business is in foreign countries, it has been hard to take any step to stop its activities.

Cultivation and Nitrogen Fertilization[1]

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It is the practice of some grape growers to make two applications of nitrogen to their vineyards, the first at plowing time, and the second near the blossoming period. The present investigation deals with the value of this second application, as indicated by the determination of nitrates in the soil under differing vineyard conditions.

The results tend to show that organic matter favors nitrate formation in soils, as does also cultivation. Early application of nitrate of soda and proper cultivation give considerable quantities of nitrates in vineyards at the time second applications are often made. Turning under cover crops in vineyards in the spring gives increased soil nitrate content. The amounts of nitrates found in well-cultivated vineyards at regular intervals during the growing season show nitrates to be present in quantity except at the start of the growing season. An application of available nitrogen at plowing time appears sufficient for properly cultivated vineyards.

AGRICULTURAL practice and scientific investigation have shown that available nitrogen is necessary for the proper growth of plants. The sources of nitrogen are soil organic matter, the air, from which nitrogen is combined and made available by bacterial activities and fertilizer materials. Publications from several of our Experiment Stations and other scientific articles give data showing that cropped soils are lower in organic matter than virgin soils. This lowering of organic matter is evidence that bacterial activities have played a large part in plant nutrition. The work of Noyes and Conner[8,*] shows a marked correlation between aerobic bacteria and the nitrification of five types of soil, variously treated with lime and fertilizer, when they were kept under conditions which eliminated some of the variables encountered in field work.

Since a large proportion of the soil nitrogen is made available through bacterial activities and bacteria have been shown to be agents for the fixation of atmospheric nitrogen, it is very important that agriculturists put into practice systems of soil management which will be favorable to the multiplication of desirable soil bacteria. Recent soil investigations tend to show that beneficial soil bacteria require oxygen, a source of carbohydrate material for their energy, and a low acid reaction of the media in which they are growing. Stated in terms of agricultural practice, this means that cultivation, organic matter, and a soil less than moderately acid are essential for desirable bacterial activities.

Nitrogen fertilization experiments can be divided into two classes on the basis of whether the plants under tests are annuals or perennials. The perennial plants, illustrated by our common fruit trees, have stored in them each fall a certain amount of reserve material in preparation for their growth the coming spring. This reserve material has not been shown to contain any large amount of available nitrogen. The atmospheric conditions of our temperate climate are usually favorable for the growth of the tree long before the soil has warmed up enough for active bacterial activities. Results where nitrate of soda has given beneficial effects on apple trees can be readily found by those desiring them. This is taken by the authors of this paper to show that the responses of perennial plants to available nitrogen early in the season are largely due to lack of sufficient bacterial activity in the cool soil at that time.

The fertilizer industry furnishes nitrogen in two forms, namely, that which is termed available and that which is termed unavailable. Out of this comes a more or less common belief that we buy some readily available nitrogen for immediate use and other nitrogen to become available and ready for use at a later date. It is well known that vegetable gardening experiments often call for applications of available nitrogen at different intervals.

We find the practice of some growers in the Chautauqua and Erie Grape Belt is to make two applications of nitrogen to their vineyards. The first application is made at plowing time and the second application occurs later near the blossoming period. The object of the work reported in this paper was to find out to what extent this second application of nitrogen fertilizer may be expected to give returns, as judged by the amount of nitrates found present in the soil under different vineyard conditions, and to see if these results correlate with other data.

EFFECT OF AMPLE AERATION

Experimental work carried on under conditions of ample aeration (because of the open nature of the soil used) is reported in Table I. The crop used was head lettuce. Samples of soil were taken every 2 wks. from November 9 to April 16. The results in crop yields, nitrates† in soil, and nitrates after incubation are given in the table.

TABLE I—CROP, NITRATES, AND NITRIFICATION ON LIGHT SANDY SOIL IN GREENHOUSE EXPERIMENTS

Applications, Rates per Acre	Weight of Crop	As Sampled	NO_3, P. p. m. on Dry Soil after Incubation[1]
Check	100	15.9[2]	374.2[2]
Nitrogen—1/3 that in 5-ton dry manure	370	8.5	386.1
Complete fertilizer elements equal 1/3 those in 5-ton dry manure	380	45.1	436.7
Complete fertilizer with nitrogen doubled	877	66.9	482.6
Double application to complete fertilizer	498	35.6	569.3
5-ton dry manure	1108	29.5	571.1
5-ton dry manure with nitrogen added	1352	66.8	577.6
5-ton dry manure with complete fertilizer	1503	54.5	717.2
Leaf mold giving equal organic matter to 5-ton dry manure	598	30.2	727.2
10-ton dry manure	1400	64.5	734.1
Leaf mold giving equal organic matter to 10-ton dry manure	841	66.2	778.1

[1] 6 wks.' incubation at 20° C. and constant moisture content with 5 cc. of 2 per cent ammonium sulfate solution.

[2] Figures are average for ten dates of sampling at 2-wk. intervals.

The results are significant. There is no case where organic matter was added in which the nitrates after incubation with ammonium sulfate were lower than a treatment where organic matter was not added to the soil. The data show that we tend to have the largest crop where organic matter is added to the soil. The nitrates in the soil for the period under investigation were doubtless affected by the growing crop; however, four out of the five highest average nitrate

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[1] Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[*] Numbers in text refer to Bibliography at end of paper.

† Soil samples taken with a bacteriologists' soil sampler described in the *J. Am. Soc. Agron.*, **7** (1915), 239. All samples were taken to the laboratory and the analysis started immediately according to the method described in THIS JOURNAL, **11** (1919), 213. The determinations were made on the moist (field) sample in every case. Moisture was determined by drying 10 g of soil to constant weight at 100° C. Nitrate results were calculated to moisture-free soil.

TABLE II—NITRATE STUDIES IN YOUNG ORCHARD HAVING DIFFERENT SYSTEMS OF SOIL MANAGEMENT[1]
(Nitrates as NO_3 per Million)

	Clean Culture Cover Crop			Accumulative Straw Mulch			Sod Several Years		
DATE	Moisture Per cent	Before Inc.	After Inc.[2]	Moisture Per cent	Before Inc.	After Inc.[2]	Moisture Per cent	Before Inc.	After Inc.[2]
8/19/14	10.2	119	201	10.6	48	262	5.0	22	170
9/16/14	14.0	102	209	17.3	168	242	15.4	47	237
11/ 9/14	18.5	11	194	23.5	28	362	19.4	4	235
6/14/15	26.6	55	318	29.8	25	234	26.5	6	303
7/ 1/15	15.0	101	249	19.8	7	426	16.5	6	290
7/27/15	15.0	88	268	17.2	60	274	15.8	9	262
8/19/15	18.9	69	238	20.5	9	289	21.5	9	268
1/24/16	22.6	26	321	23.0	33	411	24.6	23	359
5/ 2/16	21.0	0	2355	22.8	66	5017	22.7	14	4845
7/18/16	14.5	80	936	14.6	41	885	8.8	1	771
11/23/16	15.9	0	159	14.9	1	167	17.5	0	167
AVERAGE	17.5	59	495	19.5	44	779	17.6	13	719

[1] Soil was silty clay loam averaging 0.15 per cent nitrogen.

[2] 6-wk. incubation at 20° C. and constant moisture content with 5 cc. of 2 per cent solution of ammonium sulfate.

contents occur on plots receiving organic matter. This table shows, therefore, that (1) nitrates tend to increase in proportion to the active organic matter present in the soil, (2) a growing crop has an effect on the nitrates present in the soil.

COMPARISON OF SYSTEMS OF SOIL MANAGEMENT

Considerable work has been reported by C. B. Lipman,[5] Albrecht,[1] Gainey and Metzler,[3] Jensen,[4] Richardson,[9] Lyon and Bizzell,[7] Whiting and Schoonover,[12] and others on the supposed effects of different crops, associated crops, and systems of soil management on nitrate formation in the soil. The work of these investigators has been conducted under a wide range of conditions; first one factor and then another has shown itself as being of great importance when the results were summarized. So little work has been conducted where the systems of soil management known as mulch, sod, and cultivation have been compared, side by side, that the present writers have included data from an experimental orchard[13] where these systems have been practiced for several years. The differences in organic matter content between the various treatments were not considered a controlling factor, as shown by analyses given elsewhere in the bulletin.[13]

The figures reported appear in accord with the results obtained by Gainey and Metzler[3] when they compacted soil beyond a certain point and prevented active nitrification. The big difference between their results and those reported in the table above is that the low nitrate content regularly occurs on the sod plot where a natural packing of the soil has taken place. The amounts of moisture do not prevent nitrification when the soil is subjected to nitrification tests by the so-called beaker method. On the basis of these data, aeration might be assumed to account for both these results and those obtained by Gainey and Metzler.

Albrecht[1] says, "Plowing has a very significant effect toward increasing nitrates." Noyes and Conner[8] show that five soils which give a direct relationship between aerobic counts and nitrates when variously limed and fertilized failed to show the presence of nitrates after being held saturated with water for about 10 mo. Excess moisture resulting from saturation or *lack of air due to the presence of excess moisture* caused no nitrates to be found in the fully saturated soils either before or after incubation by the beaker method and this would indicate that aeration has a definite relationship to nitrification.

Lohnis[6] found that, in respect to nitrification, aeration is of great importance. Schloesing[10] in his experiments also showed that the amount of nitrate nitrogen found was in direct proportion to the amount of oxygen supplied.

ADDITION OF NITRATES

Gainey[2] gives results showing that when conditions are such that nitrification is hindered, ammonification increases. To check up this point the writers are presenting some data (Table III) secured in sodded land one month after ammonium sulfate and nitrate of soda were added in comparative tests. The soil was a silty clay and had been in sod for at least 3 yrs. It was well packed and firm; therefore the data should show the extent to which ammonium sulfate has given nitrates in excess of plant requirements under the conditions of the experiment. The check shows only a small amount of nitrates and the soil is one which is relatively high (for the locality) in volatile matter and nitrogen.

TABLE III—NITRATES IN SODDED LAND ONE MONTH AFTER APPLICATIONS OF NITRATE OF SODA AND AMMONIUM SULFATE
(Samples taken June 29, 1920)

		NO_3, P. p. m. of	Increase Due to	
Applications per Acre	Lbs.	Dry Soil	$NaNO_3$	$(NH_4)_2SO_4$
Nothing	...	9.5	...	...
Nitrate of soda	310	73.0	63.5	...
Ammonium sulfate	310	15.0	...	5.5
Nitrate of soda	620	326.0	316.5	...
Ammonium sulfate	620	23.0	...	13.5
Nitrate of soda	930	882.0	872.5	..
Ammonium sulfate	930	17.0	...	7.5

The results indicate that:

1—Nitrates in the soil increase with increased applications of sodium nitrate.

2—Ammonium sulfate, though applied in quantities equal to the nitrate of soda and carrying more nitrogen, does not nitrify readily in this compact sodded soil.

3—The soil, though high in organic matter (for the locality) and of moderate acidity, does not contain a large quantity of nitrates under field conditions.

Samples were taken from six vineyards in 1920 at the time the second application of nitrogen fertilizer is usually made (Table IV) to find out what quantities of nitrates were present in the soil from natural sources and from applications of nitrate of soda made earlier (at plowing time).

TABLE IV—NITRATES IN VINEYARD SOILS AT TIME SECOND APPLICATION OF NITRATE OF SODA IS USUALLY MADE

SOIL No.	Kind of Soil	Status of Organic Matter in Soil	Cultivation Practiced	Nitrate of Soda Lbs. per Acre	NO_3, P.p.m. of Dry Soil
1	Silty clay	Medium low	Thorough	None	352
			Thorough	767	678
2	Silt loam	Medium low	Poor	None	18
			Poor	643	121
3	Sandy loam	Average for soil type	Thorough	None	73
			Thorough	570	105
4	Silt loam	Average for soil type	Thorough	None	52
			Thorough	600	55
5	Gravel loam	Average for soil type	Thorough	None	38
			Thorough	242	33
6	Silt loam	High for locality	Fair	None	92
			Fair	564	66

On the heavy soils, 1 and 2, containing medium to low quantities of organic matter nitrates were present, but not in as great quantities as where large applications of nitrate of soda had been made at plowing time.

On the soils of medium organic matter content, 3, 4, and 5, we have again comparisons between nitrification without nitrate fertilization at plowing time and with rather heavy applications of nitrate of soda at plowing. The cultivation was well carried out and there was no great difference between the plots without and with the nitrate of soda application.

Soil 6 is comparatively virgin soil, high in organic matter, and the heavy application of 564 lbs. of nitrate of soda per acre did not give as high nitrate content to the soil on the date the samples were taken as the check.

The data show no discernible lack of nitrates present where the cultivation had been well carried out.

PLOWING IN COVER CROPS

The result of plowing under cover crops on the amount of nitrates found in the soil on different dates is given in Table V which gives the comparison of nitrates between cover crop plots and the check plot in a well-cultivated vineyard on good soil for the season of 1921. This vineyard was fertilized rather liberally early in the spring, and any increase in nitrates on the cover crop plots can therefore be directly attributed to the effects of increased bacterial activity due to readily decomposable material furnished by the cover crops. Except on June 23 the cover crop plots gave a higher nitrate content than the check. The cover crops were planted again in August, and September 1 finds that the young cover crops have apparently reduced the nitrate content to practically the same as the check plot.

TABLE V—COMPARISON OF NITRATES IN WELL-CULTIVATED VINEYARD ON GOOD GRAVEL LOAM THROUGH SEASON[1]

	May 24	June 10	June 23	July 7	July 21	Aug. 5	Aug. 19	Sept. 1	Av.
Check	39[2]	54	119	68	51	39	29	16	52
Cover crops	66	99	104	85	85	50	39	17[3]	68
Difference due to cover crop	27	45	−15	17	34	11	10	1	16

[1] 400 lbs. high-grade complete fertilizer used at plowing time.
[2] Figures are nitrates per million pounds of dry soil.
[3] Cover crops actively growing.

Without any second application of fertilizer we find in both sets of figures plenty of nitrates present during the active growing season and up to the time the cover crops are planted. An average of 52 parts of nitrates on the check plot is equivalent to 213 lbs. of nitrate of soda per acre. The average of 68 for the cover crop plots is equivalent to 281 lbs. of nitrate of soda per acre.

In summarizing this table we are led to believe that active organic matter, which serves as food for soil bacteria, increases nitrate production.

These results bear out the results of Whiting and Richmond,[11] who find that plowing under sweet clover before corn "furnishes large amounts of nitrate nitrogen for the corn crop." Calling attention to the very general agricultural practice of having corn follow the green manure crop in the rotation and the generally accepted beneficial effects of turning under a green manure crop, the data so far given in this article are confirmatory of the expressed belief that aerobic bacterial activities in the presence of a source of carbohydrate material give available plant food in quantities that produce increased crops.

COMPARISON OF ADJACENT VINEYARDS

To see what effect different systems of management have on vineyards on the same soil and adjacent to one another, the data in Table VI were procured.

On all except one date of sampling the highly cultivated vineyard had the greater amount of nitrates present in the soil. The quantities of nitrate in the highly cultivated vineyard were always ample, for the average of 53 p. p. m. is equivalent to 218 lbs. of nitrate of soda per acre. The figures for August 19 and September 1 are taken to show that the plowing done in the average cultivated vineyard about August 1 tended to increase nitrification, while a heavy natural growth of weeds serving as a cover crop decreased the nitrates present in the highly cultivated vineyard. In summarizing this table it appears that cultivation increased nitrate production.

TABLE VI—COMPARISON OF NITRATES IN ADJOINING VINEYARDS THROUGH SEASON

	May 24	June 10	June 23	July 7	July 21	Aug. 5	Aug. 19	Sept. 1	Av.
High cultivation	62[1]	60	60	58	81	46	40	21[2]	53
Average cultivation for grape belt	25	39	69	29	43	11	14[3]	17	31
Difference for high cultivation	37	21	−9	29	38	35	26	4	22

[1] Figures are nitrates per million pounds of dry soil.
[2] Cover crop of weeds.
[3] Plowed recently, turning under summer's growth of weeds.

Lyon and Bizzell[7] give data showing the effects of one crop on another as expressed in the nitrate content of the soil. Is it not significant that these beneficial effects so regularly accompany associations of crops that would not tend to impede soil aeration?

NITRATES AND MOISTURE CONTENT

Nitrates and moisture results obtained bi-weekly in 1921 are given in Table VII.

TABLE VII—NITRATES AND MOISTURE IN VINEYARDS FOR SEASON OF 1921

	NO_3, P. p. m. of Dry Soil	Sodium Nitrate per Acre to Which NO_3 Content Is Equivalent for Average Depth Sampled Lbs.	Moisture in Soil Per cent
May 6 (Plowing time)	14	58	13.2
May 24	58	238	18.3
June 10	110	452	12.5
June 23	113	464	13.7
July 7	70	288	13.1
July 21	74	304	16.3
August 5 (Cover crop sowing)	79	325	14.7
August 19	60	247	17.3
September 1 (Cover crop growing)	57	234	12.1

This table gives the results of studies carried on with twenty-four plots located on at least three distinct types of soil scattered over an area of 10 sq. mi. There was a difference of over 500 ft. in elevation between the lowest and highest plot.

The nitrate and moisture contents of the soil are given at 2-wk. intervals. The nitrates start with 14 p. p. m., the equivalent of 58 lbs. of nitrate of soda per acre, and increase until June 23 when the maximum, equivalent to 464 lbs. of nitrate of soda per acre, is reached. The data show that moisture did not bear a definite relation to the nitrate content of the soil.

These data from twenty-four plots receiving different treatments as to fertilizer but proper cultivation indicate *that applications of nitrate of soda later than May 24, 1921, would have been wasted.*

DURATION OF EFFECT OF INITIAL NITRATE ADDITION

The literature cited and the results given in the foregoing do not give information as to how far into the season the effects of the initial application of available nitrogen extend. Our measure of this has been a comparison on different dates of the nitrate content of plots where nitrate has been applied and the check plots beside them. The data for 1921 are given in Table VIII.

In all cases the nitrate of soda plots show greater nitrate content than the checks. When we consider that 100 parts of nitrate are equivalent to more nitrate of soda than

Table VIII—Comparisons of Nitrates between Checks and Applications of Nitrate at Plowing Time, Season 1921

Date	NO_3, P. p. m. Lbs. of Dry Soil Check Plots	 Nitrate of Soda Plots
May 24	35[1]	116[1]
June 10	57	262
June 23	66	192
July 7	51	102
July 21	45	94
August 5	58	160
August 19	49	92
September 1	47	100

[1] Each figure is the average of five comparisons.

an application of 400 lbs. per acre we have evidence that properly cultivated vineyards do not require nitrate of soda applications after plowing time. The check plot data are evidence that our present vineyard soils contain enough organic matter so that, with good cultivation, bacterial activities will furnish nitrates in excess of the quantities used by the growing plants.

The ratios of oxygen, carbon dioxide, organic matter, bacteria, fungi, plant food, etc., for the optimum development of any variety of plant are not known. The synopsis at the beginning of this paper gives merely indications of what the results secured may mean.

Bibliography

1—W. A. Albrecht, Missouri Agr. Expt. Sta., *Bull.* **172.**

2—P. L. Gainey, *Soil Science*, **3** (1917), 399.

3—P. L. Gainey and L. F. Metzler, *J. Agr. Research*, **11** (1917), 43.

4—C. A. Jensen, *Bur. Plant Ind., Bull.* **173.**

5—C. B. Lipman, 35th Annual Meeting, Society Promotion Agricultural Science.

6—Lohnis and Green, *Centr. Bakt. Parasitenk. II Abt.*, **37** (1913).

7—T. L. Lyon and J. A. Bizzell, Cornell Univ. Agr. Expt. Sta., *Memoir* **1.**

8—H. A. Noyes and S. D. Conner, *J. Agr. Research*, **16** (1919), 27, No. 2.

9—A. E. V. Richardson, *J. Dept. Agr. Victoria*, **11** (1913), 429.

10—T. Schloesing, *Compt. rend.*, **77** (1873), 203.

11—A. L. Whiting and T. E. Richmond, Illinois Agr. Expt. Sta., *Bull.* **233.**

12—A. L. Whiting and W. R. Schoonover, Illinois Agr. Expt. Sta., *Bull.* **225.**

13—C. G. Woodbury, H. A. Noyes and J. Oskamp, Indiana Agr Expt. Sta., *Bull.* **205.**

The Recovery of Potash as a By-product in the Blast Furnace Industry[1,2]

By William H. Ross and Albert R. Merz[3]

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The weighted average of the potash in the ores, coke, and limestone used in the blast furnace industry amounts to approximately 0.2 per cent for each material, which is less than one-third as great as that found for the raw mix used in the cement industry. In the case of the ores the potash ranges from 0.05 per cent for Mesaba ores to over 2 per cent for certain foreign ores. As the consumption of high potash ores is relatively small as compared with low potash ores, the weighted average of the potash in the ores consumed is less than the mean average found for different ore samples. On the basis of weighted averages the total potash in the ore, coke, and limestone used in blast furnaces amounts, respectively, to 7.2, 1.9, and 4.9 lbs. per ton of pig iron, or to a total of 14.0 lbs. The potash in the slag amounts to 8.4 lbs. which leaves a balance for the potash volatilized of 5.6 lbs. per ton of pig iron. This amounts to a total for all plants of about 100,000 tons annually as compared with 87,000 tons for the cement industry. As there are twice as many blast furnaces as cement plants in the United States, the quantity of potash lost per individual plant must therefore be less in the blast furnace industry than in the cement industry, but it is possible that the dust from some blast furnaces in which manganiferous or southern ores are used may be richer than the richest cement dust.

In a previous publication[4] an account is given of a survey that was made of the potash that escapes from the cement plants of the country. Representative samples of raw mix and of the corresponding ground clinker were collected from all but four of the cement plants then operating. By determining the potash content of these different samples and knowing the ratio of raw mix to ground clinker, it was possible to make a close estimate of the potash lost from each individual plant. The results obtained varied from 0.35 to 5.14 lbs. of potash per bbl. of cement produced, with an average for all plants of almost 2 lbs. On the basis of an average production of 90,000,000 bbls., the total potash escaping from all the cement plants of this country was estimated to amount to about 87,000 tons annually. Since these estimates were made, installations have been placed in a number of plants for the recovery of this potash, and in every case the quantity that was found to escape from the kilns closely agreed with the estimates that had been made during the course of the survey. It is therefore logical to assume the reasonable correctness of the total estimate that was made for all the plants of the country.

Method of Investigation

On the completion of this investigation a corresponding survey was undertaken of the potash that escapes from the blast furnaces of the country. Through the coöperation of Mr. Frederick Crabtree of the Bureau of Mines a systematic collection was made of iron ore, coke, and limestone samples which represented the principal districts now producing these materials for use in blast furnaces. Each of the samples was analyzed for potash by at least two chemists. From the data thus obtained, it was possible to calculate the quantity of potash that was charged into a blast furnace during any period if the source and consumption of the materials used in the charge were known. This quantity less that which was lost in the slag gave the total potash that escapes from the furnace. Information on the average amount of potash lost in the slag was secured by analyzing a large number of samples collected from many of the leading blast furnaces of the country.

Results

The results obtained and summarized in Tables I and II show that the potash content of the numerous samples of ore, coke, and limestone that were analyzed give a weighted average about the same for each material, which amounts to approximately 0.2 per cent. In the case of the ores the potash ranged from a minimum of 0.05 per cent for some Lake Superior ores to over 2 per cent for certain foreign ores. As shown in Table I, samples from the Menominee and Marquette ranges contained between two and three times as much potash as those from the Mesaba range. The potash in the ores from the same range agreed so closely that no material difference was found between the mean and weighted averages for any range. This close agreement prevailed both for Bessemer and non-Bessemer ores.

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[1] Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published by permission of the Secretary of Agriculture.

[3] Analyses by William Hazen, R. M. Jones, T. R. LeCompte, W. B. Pope and G. J. Hough.

[4] William H. Ross, Albert R. Merz and C. R. Wagner, "The Recovery of Potash as a By-product in the Cement Industry," *U. S. Dept. Agr., Bull.* **572** (1917), 1.

Southern and imported manganiferous ores are usually richer in potash than the Lake Superior ores. The imported manganiferous ores vary very greatly in potash content, some being as low as those from the Mesaba range, but the average for these ores is greater than for any of the domestic ores excepting those from the Georgia district.

TABLE I—POTASH IN DOMESTIC AND FOREIGN ORES

SOURCE OF ORE	Production and Importation in 1920[1] Gross Tons	Ores Analyzed	Total Samples Analyzed	Potash (K_2O) Weighted Average Per cent
Mesaba range	36,641,880	76	126	0.09
Gogebic range	8,298,206	26	46	0.10
Menominee range	5,651,542	26	36	0.28
Marquette range	4,457,609	22	31	0.23
Cuyuna range	1,757,775	8	8	0.10
Vermillion range	1,053,518	4	9	0.11
Alabama	5,894,011	6	8	0.55
New York	920,009	3	3	0.10
Virginia	320,924	4	4	0.32
New Mexico	274,219	5	5	0.10
Georgia	104,511	3	3	0.82
Miscellaneous domestic	2,230,261	10	11	0.51
Foreign non-manganiferous	1,273,456	5	6	0.14
Foreign manganiferous	600,000[2]	11	22	0.77
WEIGHTED AVERAGE FOR ALL ORES				0.19

[1] Geol. Surv., "Mineral Resources," **1920** (1922), Part I.
[2] Estimated.

It happens, however, that the consumption of southern and manganiferous ores in this country is only about 10 per cent of the total, while the production from the Menominee and Marquette ranges is less than one-third as great as that from the Mesaba range. The weighted average of the potash in the ores consumed in this country is therefore less than the value obtained for the mean average of potash in different ore samples. According to the results reported in the Department of Agriculture bulletin already referred to, the potash in the raw mix of cement plants varied at the time of the survey from 0.2 to 1.16 per cent, with a weighted average for all the plants of 0.67 per cent. The average percentage of potash in the raw mix used in cement manufacture is therefore over three times as great as that occurring in the raw materials consumed in the blast furnace industry.

TABLE II—ESTIMATED LOSS OF POTASH IN BLAST FURNACE INDUSTRY

MATERIAL	Consumption in 1920[1] Short Tons	Average Potash (K_2O) Content Per cent	Total Potash (K_2O) Content Short Tons	Pounds Potash (K_2O) per Ton of Pig Iron
Iron ore	77,800,000	0.19	147,820	7.2
Limestone	20,000,000	0.20	40,000	1.9
Coke	42,000,000	0.24	100,800	4.9
TOTAL IN CHARGE			288,620	14.0
	Production 1920			
Pig iron	41,300,000			
Slag	31,000,000[2]	0.56	173,600	8.4
TOTAL LOST BY VOLATILIZATION			115,020	5.6

[1] Geol. Surv., "Mineral Resources," **1920** (1922), Part I.
[2] Estimated.

In an investigation that was made some time ago by R. J. Wysor[5] of the Bethlehem Steel Co., it was reported that the potash in the ore, coke, and limestone used at that plant amounted, respectively, to 10.3, 5.8, and 6.3 lbs. per ton of pig iron, or to a total of 22.4 lbs. per ton.

The results given in Table II, which have been obtained for numerous other plants throughout the country, show corresponding values of 7.2, 1.9, and 4.9 lbs. per ton of pig iron, or a total of 14.0 lbs. The average potash in the slags, on the other hand, was found to be almost twice as great as reported by Wysor for the Bethlehem Steel Company. It therefore follows, as Wysor himself predicted, that the potash volatilized per ton of pig iron must be less for the average plant than was found for the Bethlehem plant. According to our results this amounts to only 5.6 lbs. per ton of iron as compared with Wysor's 17.9 lbs.

That the potash lost at the Bethlehem plant is about three times greater than the average for the blast furnaces of the country as a whole is further indicated by the potash found in the dust collected in the stoves and boilers of different plants. The average given by Wysor for dusts collected at the Bethlehem plant amounted to 9.9 per cent. The average value which we have found for the potash in sixty-six samples of dust collected at various other plants amounts to only 3.3 per cent, or one-third of that for the Bethlehem plant.

If our value of 5.6 lbs. be taken as the average quantity of potash volatilized per ton of pig iron and an average normal production of iron of 36,000,000 short tons be assumed, then the total potash volatilized from the blast furnaces of this country will amount to about 100,000 tons, as compared with the 87,000 tons found for cement plants. As there are twice as many blast furnace plants as cement plants in the United States the quantity of potash lost per individual plant must therefore be less in the blast furnace industry than in the cement industry.

POSSIBILITY OF RECOVERY

When the survey was made of the cement industry it was recognized that the dust from some plants was probably too low grade ever to be used as a source of potash even if no cost were involved in collecting the dust. The richness of the dust in other plants indicated, on the other hand, that potash could be profitably recovered from this source, particularly if some inexpensive means were installed along the lines of the process now in operation at the Santa Crux plant whereby a mechanical separation of the potash and the dust is brought about during the process of collection.

In the blast furnace industry the greater part of the volatilized dust is now lost in the primary washers. The possible recovery of dust in this industry is therefore dependent on the substitution of a dry system of purifying the gases in place of the present wet system. Judging from results that have already been obtained in several plants with two dry cleaning systems of entirely different design it is possible that a substitution of a dry system for the present wet system may ultimately be made in many blast furnace plants. Owing to the low potash content of the materials used in some plants it will no doubt be found that the dust from these plants if collected will be too low grade to be used as a source of potash unless it is found to contain other products of value which will contribute to the cost of concentrating the potash. The situation with respect to plants operating on manganiferous, southern, or Menominee ores should be entirely different. Owing to the richness of these ores it is possible that the dust from these plants will be found to be richer than the richest cement dust.

It may further be emphasized that if dry systems are eventually installed for purifying blast furnace gases the collected dust, although possibly not extensively used as a source of potash under normal conditions, might nevertheless serve as an important potential source of potash which would be immediately available in case of a future emergency.

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[5] *Bull. Am. Inst. Mining Eng.*, **121** (1917), 1.

Tests of an Iodine Pentoxide Indicator for Carbon Monoxide[1,2]

By S. H. Katz[3] and J. J. Bloomfield[4]

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The "Hoolamite" or activated iodine pentoxide indicator for carbon monoxide[5] is frequently used by engineers of the Bureau of Mines engaged in mine-rescue and recovery operations. The tests described in this paper were made to determine its accuracy.

The indicator gives positive indications for carbon monoxide in air in concentrations of 0.07 per cent or more. In a few instances there were no indications with 0.07 and 0.08 per cent. No failures to indicate occurred at higher concentrations. Two tests with 0.10 per cent CO in air indicated 0.10 and 0.05 per cent; eight tests with 0.15 per cent gas gave determinations ranging from 0.10 to 0.23 per cent, with an average of 0.16. At higher concentrations the variations were proportionally about the same.

The results of tests with air containing wood smoke and with flue gases averaged a little high. Low oxygen or high carbon dioxide in the gas tested did not decrease the action of the Hoolamite.

No differences were found in tests made at ordinary or freezing temperatures, in daylight, or in artificial light.

Acetylene, alcohol, ammonia, benzene, ether, ethylene, gasoline, hydrogen chloride, hydrogen sulfide, natural gas containing members higher than methane, and water produce interfering effects if allowed o enter the sensitive material. When the gases are first passed through the fresh activated charcoal, interfering substances are absorbed and no error results from their presence. Carbon dioxide, carbon tetrachloride, chlorine, methane, nitrogen peroxide, phosgene, and sulfur dioxide do not interfere.

Determinations of carbon monoxide are easily made in less than one minute, and no skill is required. Only one person in thirty has been found to have difficulty in determining the color shades. The instrument is proving a valuable aid in mine-rescue and recovery operations after fires and explosions, and for testing air around blast furnaces, gas producers, water-gas and coal-gas plants, and other places where carbon monoxide occurs. It also may be used to promote furnace economy by indicating carbon monoxide in flue gases.

HOOLAMITE is a mixture of iodine pentoxide and fuming sulfuric acid on granular pumice stone. In contact with carbon monoxide, it changes—owing to the liberation of iodine—from the original white to increasing depths of bluish green, then violet-brown, and finally black, depending upon the concentration of carbon monoxide.

The indicator (Type B, Figs. 1 and 2, in article by Hoover[5]) consists of a tube of activated charcoal, through which gas is drawn by means of a rubber hand bulb. It then discharges through a small glass tube containing Hoolamite. The charcoal removes any gas other than carbon monoxide which may produce a false test, unless it is present in large quantity. Interfering dusts and mists are stopped by cotton-wool filters, after the charcoal and before the Hoolamite. Five permanent colors on pumice stone are placed for comparison in a sealed glass tube alongside the Hoolamite.

According to the patents,[6] Hoolamite may consist of:

	Per cent
Iodine pentoxide, 10 parts	11
Fuming sulfuric acid, 50 parts (60 per cent SO_3)	55
Pumice granules, 30 parts (20 to 40 mesh)	33
Iodine, 0.25 to 2 per cent	0.25 to 2

A larger proportion of fuming acid is claimed to increase the sensitivity, and the iodine is added for the same purpose.

Analysis[6] of some of the material used in these tests gave 12.29 per cent iodine pentoxide, 51.89 per cent fuming sulfuric acid (47 per cent SO_3), and 35.82 per cent pumice granules. No free iodine was detected.

Since moisture causes deterioration of the Hoolamite, it is put up in small glass tubes tapered at the ends and sealed. The tips are easily broken open with the fingers.

In using the detector, the bulb is squeezed three times, the tube of Hoolamite is inserted, the bulb is squeezed 10 times more (10 squeezes of the bulb deliver 350 ± 50 cc. of gas), and the carbon monoxide is estimated. Should the color be indistinct, 20 squeezes are advisable. The carbon monoxide is then placed at half the corresponding shade for 10 squeezes.

Tests for CO in Air

Table I gives the results of tests with CO-air mixtures. Fig. 1 shows the averages of determinations, compared graphically with results of Haldane analyses.

Less than 0.07 per cent of CO in air gave no noticeable color change; in a few instances there was no indication with 0.07 or even 0.08 per cent, but no failures to indicate were found in concentrations higher than these. Of two tests with 0.10 per cent CO, one indicated only 0.05 per cent. Eight tests with 0.15 per cent gave determinations ranging from 0.10 to 0.23 per cent. At higher concentrations the deviations were proportionally about the same as those mentioned. The averages of several determinations

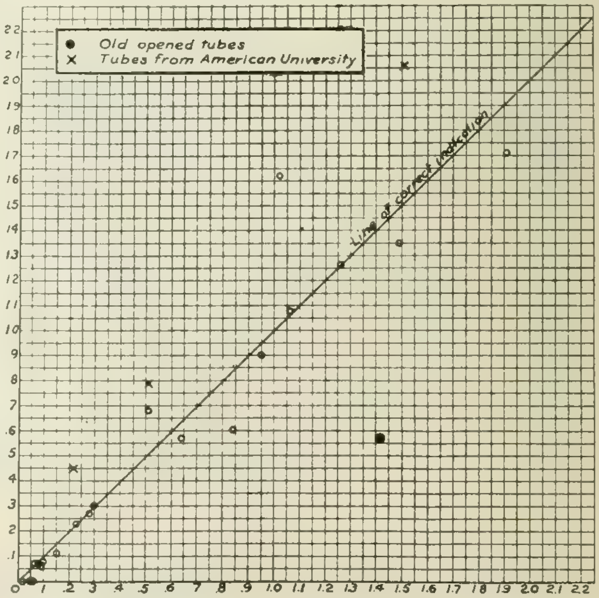

FIG. 1—AVERAGES OF CARBON MONOXIDE DETERMINATIONS WITH INDICATOR COMPARED TO ANALYSES WITH HALDANE APPARATUS

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[1] Received June 22, 1921.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Assistant Physical Chemist, Pittsburgh Experiment Station.

[4] Junior Chemist, Pittsburgh Experiment Station.

[5] C. R. Hoover, "The Detection of Carbon Monoxide," THIS JOURNAL, 13 (1921), 770.

[6] A. B. Lamb and C. R. Hoover, "Absorbent," U. S. Patent 1,321,061, Nov. 4, 1919; "Gas Detector," U. S. Patent 1,321,062, November 4, 1919.

[7] Analysis by W. A. Selvig.

Table I—Results of Determinations of CO in Air

(CO₂ contents approximately one-fifth those of CO. Bulb squeezed 10 times unless otherwise stated)

Test No.	CO by Haldane Analysis Per cent	CO by Indicator Per cent	Observer No.	Remarks
18	0.02	0.00	3	
19	0.02	0.00	10	
20	0.02	0.00	3	
57	0.05	0.00	3	20 squeezes
58	0.05	0.00	7	
59	0.05	0.00	3	
60	0.06	0.00	3	20 squeezes
61	0.06	0.00	17	
15	0.07	0.10	10	
16	0.07	0.00	11	
17	0.07	0.10	3	
25	0.07	0.11	3	20 squeezes
26	0.07	0.11	7	
27	0.07	0.09	3	
62	0.07	0.05	10	
66	0.07	0.00	16	Av. 8 tests = 0.07 per cent
63	0.08	0.09	3	20 squeezes
67	0.08	0.00	16	
83	0.08	0.10	7	
84	0.08	0.10	4	
85	0.08	0.10	4	Test at 0° C.
86	0.08	0.08	9	
87	0.08	0.05	3	20 squeezes
88	0.08	0.04	4	20 squeezes, test at 0° C. Av. 8 tests = 0.07 per cent
64	0.09	0.075	4	20 squeezes
68	0.09	0.05	3	Av. 2 tests = 0.06 per cent
65	0.10	0.12	15	20 squeezes
69	0.10	0.05	4	Av. 2 tests = 0.09 per cent
49	0.15	0.10	3	
50	0.15	0.16	4	
51	0.15	0.10	4	
52	0.15	0.23	3	Test made in artificial light
53	0.15	0.23	4	
54	0.15	0.16	7	
55	0.15	0.16	5	
56	0.15	0.10	5	Av. 8 tests = 0.16 per cent
40	0.22	0.45	3	Old tubes from Chemical Warfare Service
41	0.22	0.45	3	
12	0.23	0.23	5	
13	0.23	0.23	4	
14	0.23	0.23	3	Av. 3 tests = 0.23 per cent
79	0.28	0.34	4	
80	0.28	0.34	4	
81	0.28	0.23	3	Test at 0° C.
82	0.28	0.16	7	
				Av. 4 tests = 0.27 per cent
9	0.30	0.23	3	
10	0.30	0.34	10	
11	0.30	0.34	3	
32	0.30	0.23	3	Tube used day previous, rubber capped 24 hrs.
33	0.30	0.34	14	
				Av. 5 tests = 0.30 per cent
28	0.56	0.23	3	Old tubes from Chemical Warfare Service
29	0.56	0.34	3	
38	0.56	1.80	3	
39	0.56	0.68	3	
				Av. 4 tests = 0.76 per cent
75	0.64	0.45	3	
76	0.64	0.45	3	
77	0.64	0.68	3	Test at 0° C.
78	0.64	0.68	3	
				Av. 4 tests = 0.57 per cent
6	0.84	0.45	16	
7	0.84	0.68	7	
8	0.84	0.68	3	Av. of 3 tests ≐ 0.60 per cent
36	0.95	0.90	11	Tube used day previous, rubber capped 24 hrs.
37	0.95	0.90	3	
72	0.97	1.44	3	
73	0.97	1.80	4	
74	0.97	1.62	4	Test at 0° C. Av. 3 tests = 1.44 per cent
21	1.06	1.08	7	
22	1.06	1.08	3	
23	1.26	1.26	3	
24	1.26	1.26	13	
34	1.42	0.45	4	Tubes used previous day, rubber capped 24 hrs.
35	1.42	0.68	3	
				Av. 2 tests = 0.57 per cent
3	1.49	1.35	1	
4	1.49	1.35	3	
5	1.49	1.35	5	Av. 3 tests = 1.35 per cent
30	1.51	2.06	5	Old tubes from Chemical Warfare Service
31	1.51	2.06	7	
1	1.91	1.35	3	
2	1.91	2.06	14	Av. 2 tests = 1.72 per cent

with newly opened tubes, as shown in Fig. 1, in general were closely correct; the greatest deviation was in the case where three tests with 0.97 per cent carbon monoxide gave an average indication of 1.62 per cent.

The data in Table I were obtained in many instances with tubes used repeatedly after fading from previous use. Used tubes were apparently as good for six or eight determinations as fresh ones, but thereafter the absorbed water showed a distinct darkening at the inlet end. Tubes that after use had been kept over night, capped with tight rubber caps, generally were found to give accurate determinations, but in one instance results were too low. Tubes that had been kept capped a week lost much sensitivity.

Tests indicated by crosses in Fig. 1 were made with a few old tubes that had been prepared by the Chemical Warfare Service three years before. Results were less uniform, though generally their sensitivity was higher than that of the tubes now made commercially.

Tests at freezing temperature and those made in artificial light were as accurate as those made under ordinary conditions. None of the twenty-six persons who made tests had any difficulty in distinguishing the shades, though it has been stated that one man could distinguish no color for carbon monoxide below 0.20 per cent.[8]

TESTS FOR CO IN SMOKE

Since gases, vapors, and smoke from fires may contain many organic compounds which can produce the colors, a test was made of the instrument for determining carbon monoxide in wood smoke. The smoke was so dense that it was impossible to see more than two feet through it. Two Haldane analyses showed 0.29 per cent carbon monoxide, while the indicator gave the following results:

Observer No.	3	7	16	12	12	8	2
Estimated CO, per cent	0.34	0.23	0.45	0.45	0.45	0.45	0.34
AVERAGE	0.39						

The average of 0.39 per cent is 0.10 per cent more than the Haldane analysis, but the difference is not much larger than shown by some of the previous tests. All observers determined the concentrations as within the two near shades of the scale used.

TESTS WITH FLUE GASES

Flue gas differs from those preceding in that it contains comparatively high proportions of carbon dioxide and low oxygen; in the previous tests, the oxygen was high and carbon dioxide low. The gases tested below were taken from the breaching of a boiler furnace. Some carbon monoxide was added to one sample in order to give higher percentage than the furnace delivered. An analysis by the Haldane apparatus gave 0.01 per cent CO, 7.98 per cent CO_2, 10.98 per cent O_2, and 81.03 per cent N_2. Results by the indicator were:

Observer No.	3	16	3	9
Squeezes	10	10	20	20
Analysis by indicator, per cent	0.00	0.00	0.05	0.05
AVERAGE	0.025			

In another test, the Haldane apparatus gave 0.22 per cent CO, 5.41 per cent CO_2, 13.66 per cent O_2, and 80.71 per cent N_2, and results by the indicator were:

Observer No.	3	4	18	20	22	19	23	21	24
Squeezes	10	10	10	10	10	10	10	10	10
Analysis by indicator, per cent	0.34	0.34	0.23	0.34	0.23	0.34	0.23	0.23	0.23
AVERAGE	0.28								

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[8] D. Harrington and B. W. Dyer, "Test of a Carbon Monoxide Detector Which Shows Green When That Gas Is Present, *Coal Age*, **19** (1921), 269.

The first gas with 0.01 per cent carbon monoxide gave tests with twenty squeezes which two observers considered positive, but less in color than the lowest shade of the scale. None of the previous tests gave positive indications with less than 0.07 per cent carbon monoxide. Tests with 0.22 per cent carbon monoxide ranged from 0.23 to 0.34 per cent by the indicator; the average of 0.28 per cent may be considered satisfactory agreement.

Since flue gas containing very low oxygen was not available, synthetic mixtures of carbon monoxide with carbon dioxide and with nitrogen were tested. Results are:

Analysis by Haldane apparatus, per cent	CO_2, 93.29		CO, 0.22	O_2, 1.49		N_2, 5
Observer No.	3	25	16	20	4	26
Squeezes	10	10	10	10	10	10
Analysis by indicator, per cent	0.28	0.23	0.28	0.23	0.34	0.23
AVERAGE, PER CENT	0.27					

Analysis by Haldane apparatus, per cent	CO_2, 1.02		CO, 0.11	O_2, 5.78		N_2, 93.09
Observer No.	3	16	9	20	4	23
Squeezes	10	10	10	10	10	10
Analysis by indicator, per cent	0.16	0.16	0.20	0.23	0.16	0.16
AVERAGE, PER CENT	0.18					

The determinations are higher on the average than those made with air containing similar quantities of carbon monoxide; however, the errors are not excessive. These tests show especially that low content of oxygen in the gas does not reduce the action.

TESTS IN MINES

Harrington and Dyer[8] tested for carbon monoxide in burning coal and metal mines, at the same time taking samples of the atmosphere which were later analyzed on Haldane apparatus. Their results are given in Table II.

TABLE II—RESULTS OF DETERMINATIONS OF CARBON MONOXIDE IN BURNING MINES

CO by Indicator Per cent	CO by Haldane Apparatus Per cent
Tests Made in Metal Mine	
0.5	0.35
0.5	0.26
0.5	0.35
0.5	0.38
0.1	0.11
0.1	0.18
0.0	0.07
0.0	0.06
Tests Made in Coal Mine	
0.0	0.01
0.0	0.03
0.1	0.13
0.2	0.11

One man of four who made the observations was unable to agree with the others regarding colors, and could see no color developed in carbon monoxide that indicated 0.20 per cent or less. This is the only instance among observations by a total of thirty persons, reported in this paper, in which material differences in observations have occurred.

It is evident that among the results in Table II, no attempt was made to interpolate between the divisions of the scale; however, the results compare favorably with those made in the laboratory under best conditions for observation.

INTERFERING GASES

Tests were made to determine whether oxidizable or strongly reactive gases and vapors, other than carbon monoxide, affect Hoolamite. In most cases, concentrations of the gases were not actually determined, the tests being made with air mixed with the gas near the source of liberation from a tank or evolution by chemical reaction. Vapors were taken from within the necks of bottles containing liquids. Trials were made with and without the charcoal guard.

Acetylene, alcohol, ammonia, benzene, ether, ethylene, gasoline, hydrogen chloride, hydrogen sulfide, and natural gas containing some higher hydrocarbons, colored the Hoolamite; when the charcoal was interposed between the Hoolamite and source of gas, no colors developed. In their patent specifications, Lamb and Hoover say that phosphine and arsine produce color.

Carbon dioxide, carbon tetrachloride, chlorine, hydrogen, methane, nitrogen peroxide, phosgene, and sulfur dioxide gave no interference.

Of the organic compounds capable of oxidation, all except methane, which is most stable generally, acted on the Hoolamite. The noninterference of methane was to be desired because of its presence in mine atmospheres, and in products of combustion in which tests for carbon monoxide are frequently made. While the tests proved that paraffin hydrocarbons higher than methane are reactive, they do not determine whether the reaction starts with ethane, propane, or butane. From the results it may be expected that all other organic gases or vapors of the aliphatic and aromatic series, when sufficiently concentrated, will interfere with tests if allowed to enter the Hoolamite, but fresh activated charcoal prevents interference. Of the inorganic gases and vapors, ammonia, hydrogen sulfide, and hydrogen chloride gave interferences when charcoal was absent.

The results show that Hoolamite may be adapted for determining many gases and vapors besides carbon monoxide.

To determine how long a 25-cc. charge of activated charcoal would restrain interfering gases, charges were tested by passing a uniform mixture of hydrogen sulfide and air through the charcoal until hydrogen sulfide appeared in the outgoing gas, as indicated by decolorization of a starch iodine solution. Concentration of hydrogen sulfide in air was 0.10 per cent, and the rate of flow, 1 liter per min., corresponding roughly to the rate when using the indicator. Methods of controlling the concentration and flow were those used in testing gas-mask canisters.[9]

The charge withheld all the hydrogen sulfide for 100 min., that is, from 100 liters of the gas mixture. Thus a charge of charcoal is good for at least one hundred tests.

Similar life tests of charcoal were made with natural gas mixed with air in different proportions; at least 9 per cent by volume of the natural gas in air was required to give a positive indication even without charcoal. When charcoal was interposed before the Hoolamite and 15 per cent natural gas in air was passed through it at a rate of 1 liter per min., no coloration of Hoolamite developed in 1 hr. When pure natural gas was passed through charcoal at the same rate, color developed in Hoolamite after 12 min., although combustible gas came through the charcoal during the whole period.

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[9] A. C. Fieldner, G. G. Oberfell, M. C. Teague and J. N. Lawrence, THIS JOURNAL, **11** (1919), 519.

Wrought Iron Pipe

A bulletin which has been issued by the Reading Iron Company combines advertising with much useful and interesting information. There is a very readable sketch of the development of the wrought iron industry from the time when the savage first discovered the possibility of beating out weapons stronger than wood and less cumbersome than stone. The puddling process is described in detail and illustrated with diagrams and photographs, as are also the later steps in the manufacture of wrought iron pipe. The requisites of a metal pipe are discussed, together with the relative value of steel and wrought iron in making welded pipe.

New Solvents for Rosin Extraction[1]

By **H. K. Benson**[2] and **A. L. Bennett**

LABORATORY OF INDUSTRIAL CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

When resinous wood of pulp size is treated at 70° C. with eight times its weight of 5 per cent ammonium hydroxide for 10 hrs., 94.5 per cent of the rosin is extracted. The ammonia extract decomposes slowly in the air at ordinary temperatures; at 90° to 100° C. it is rapidly and completely decomposed, yielding ammonia vapor and finely divided rosin and humus in suspension. Rosin and humus may be separated by gasoline. None of the solvent is retained in the humus after heating.

Wood chips saturated with ammonia solution give off the ammonia completely when steam-distilled.

Denatured ethyl alcohol at a dilution of 70 per cent is as efficient a solvent for rosin as ammonia, benzene, turpentine or petroleum ether.

THE use of ammonia as a solvent for rosin has been described in a previous article,[3] the resinous wood having been reduced to sawdust, shavings, and small chips previous to its extraction. In view of the rapidly increasing proportion of coniferous woods in pulp manufacture it seemed advisable to determine the efficiency of ammonia as an extraction agent in the case of pulp chips and to compare it with other solvents which might be used.

EXPERIMENTAL

The resinous wood was hogged to pulp size (1-1/8 in. × 3/4 in. × 3/32 in.), placed in pressure bottles, covered with the solvents, and placed in a thermostat at 70° C. for 5 hrs. The extraction liquor was next drained off, the chips washed, and the combined liquors evaporated until all solvent was removed, leaving "humus" and rosin in the case of ammoniacal extraction and rosin alone in the other samples. The humus and rosin were separated by dissolving the rosin in petroleum ether, filtering off the humus, and evaporating to dryness to recover the rosin. The efficiency of extraction was determined by drying the extracted wood at 100° C., grinding it to fineness in a Grumbaugh mill, and extracting in a Soxhlet apparatus. The results obtained are given in Table I. A 50-g. sample was used in each case.

TABLE I—COMPARATIVE EFFICIENCY OF ROSIN SOLVENTS

Expt. No.	Solvent	Volume Cc.	Washing Cc.	Washing Per cent	Extraction of Rosin Per cent	Soxhlet Per cent	Efficiency Per cent
1	Turpentine	200	50	..	20.10	24.35	45.2
2	Benzene	200	50	..	17.86	26.85	40.0
3	Petroleum ether	200	50	..	17.01	21.25	44.4
4	Ammonium hydroxide	400	200	1	16.51	20.13	45.0
5	Ammonium hydroxide	400	200	1	17.00	25.05	40.5
6	88% alcohol	200	50	88	15.46	22.60	40.3
7	70% alcohol	200	50	70	16.52	22.05	42.8
8	50% alcohol	200	50	50	14.71	27.60	34.7

The effect of length of time and size of wood on extraction of rosin is given in Table II. The volume of alcohol used was 200 cc. and of ammonium hydroxide 400 cc. in each case, the chips being washed as before.

DECOMPOSITION OF AMMONIA EXTRACTS—When the solutions obtained from the ammonia extraction were left standing in the air, the color changed from a light cream to dark brown. By raising the temperature evenly at the rate of 5° C. every half hour and absorbing the ammonia in wash bottles, the quantity of ammonia given off was estimated.

TABLE II—EFFECT OF TIME AND SIZE OF WOOD ON EXTRACTION

Solvent	Concentration (Per cent Volume)	Size of Wood Inches	Time Hrs.	Extraction of Rosin Per cent	Soxhlet Per cent	Efficiency Per cent
Alcohol	88	1 × 1/8 × 1/8	5	26.40	13.8	65.7
	70	1 × 1/8 × 1/8	5	31.96	12.8	71.7
	50	1 × 1/8 × 1/8	5	17.41	21.8	44.5
Ammonium hydroxide	5	1 × 1/8 × 1/8	5	32.2	6.1	83.9
	5	1-1/8 × 3/4 × 3/32	5	30.1	8.2	78.5
	5	1 × 1/8 × 1/8	10	25.65	1.6	94.5
		1-1/8 × 3/4 × 3/32	10	28.89	5.8	83.3

The results are plotted against the temperature in Fig. 1. Rapid decomposition took place at 93° to 100° C. When slowly heated, ammonia was not given off below 80° C. and at 100° C. none remained.

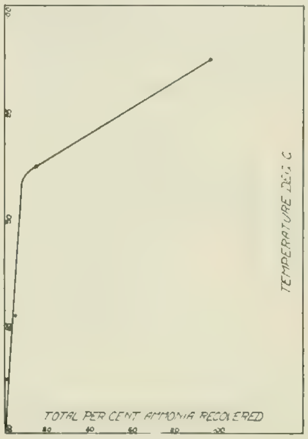

FIG. 1

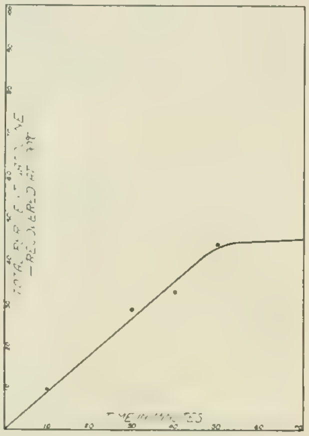

FIG. 2

LOSS OF SOLVENTS IN HUMUS—The extraction residue after the ammonia had been driven off consisted of rosin and humus of tar-like consistency. When treated with gasoline, benzene, or some similar solvent the rosin dissolved, leaving the humus as a residue. This was removed by filtration and dried to a fine powder. Humus in the dry state was saturated with solvent; after draining off the latter, the bottle containing the humus with adhering solvent was weighed to determine the weight of solvent absorbed. It was next heated in an oven at 100° C. for 10 min.; then allowed to cool in a desiccator containing an atmosphere of vapor of the solvent used, and weighed. From a succession of such weighings, the rate and extent of removal of solvent from the humus were determined. The results in the case of gasoline are shown in Fig. 2. The gasoline used for this purpose showed by the Bureau of Standards method of analysis that 44 per cent was volatile at 100° C. or below. Inasmuch as the curve shows likewise that 44 per cent of the gasoline is volatilized by heating the humus for 50 min. at 100° C. none of the solvent was retained by the humus.

AMMONIA RECOVERY—The liquor from an ammonia extraction was distilled slowly and the vapors absorbed in 1:3 sulfuric acid. The waste liquor was treated in the same manner. The extracted wood chips were steam-distilled and the condensate redistilled and absorbed in acid. The results, given in Table III, show that although 3.12 per cent ammonia remains in the wood, it can be completely recovered.

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[1] Received August 4, 1921.

[2] Professor of Chemical Engineering.

[3] THIS JOURNAL, 7 (1915), 918.

TABLE III—AMMONIA RECOVERY

Ammonia Used	NH_4OH Grams
400 cc. 5% ammonium hydroxide	20
200 cc. 2.5% ammonium hydroxide	5
TOTAL	25
Ammonia Recovered	
Extract liquor	18.65
Wash liquor	5.49
Wood (steam distillate)	0.78
TOTAL	24.92

DISCUSSION OF EXPERIMENTAL RESULTS

The results obtained from the first series of extractions (Table I) show that under the conditions of these tests ammonia is not an efficient solvent for rosin contained in wood chips of pulp size. Inasmuch as the temperature of extraction cannot be increased and previous studies have shown that increasing concentration is no aid, increase of time is the only variable factor. As shown in Table II, by doubling the time of digestion the larger chips may be extracted as completely as the smaller size.

A comparison in the efficiency of various solvents under the same conditions shows that 70 per cent denatured alcohol is of the same order as the more generally used volatile oils. Inasmuch as this is a product which might well be an end-product in the use of the extracted chips in hydrolysis or in sulfite pulp, it seems peculiarly advantageous because its recovery would utilize the same methods and equipment as are employed in its production.

Although no extractions were made by employing other alkaline solutions, such as sodium and potassium hydroxides, the results of commercial practice in the soda process of pulp manufacture from resinous woods show practically complete removal of rosin. Similar results were obtained by Bates,[4] showing that the efficiency of rosin extraction with sodium hydroxide in the case of resinous pine is 95 to 97 per cent where the chips are thoroughly washed. Its disadvantage as a purely rosin solvent lies in the difficulty of recovering rosin from the soda liquor. This is obviated by the use of ammonia because of the ease with which the ammonium product is decomposed by heat, and the rosin subsequently recovered.

Objections to the use of ammonia as a solvent for rosin have been made on account of the necessary use of gasoline for the separation of humus from the rosin and on account of the retention of ammonia in the chips. The analytical data in this study show that the humus, relatively small in quantity, does not retain any appreciable quantity of a low boiling solvent, and that steam distillation will effectively remove all but traces of ammonia from the wood chips. The absorption and concentration of ammonia involve no problem.

[4] THIS JOURNAL, **6** (1914), 289.

Analytical Determination of Oxides of Nitrogen in Gas Mixtures[1,2]

By Charles L. Burdick

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The following paper describes a simple method of determining oxides of nitrogen in gas mixtures by washing the gas in dilute alkali. A theoretical consideration of the reactions involved is included.

IN connection with an investigation of the equilibrium between aqueous nitric acid, nitrogen peroxide and nitric oxide[3] and the study of the rate of reaction and catalysis of the oxidation of nitric oxide,[4] it became necessary to devise a method for the determination of the nitrogen oxide content and the degree of oxidation of a mixture of oxides of nitrogen diluted with nitrogen or air. It was found in the laboratory work that washing of a measured volume of the gas in dilute alkali afforded the simplest and most accurate means of determination of the gas compositions. The later work which served to develop the method as a means of technical control analysis was carried out in connection with a study of the performance of nitric acid absorption towers at the Sheffield Experiment Station at U. S. Nitrate Plant No. 1.

The reactions representing the mechanism of the absorption of nitrogen peroxide or mixtures of nitrogen peroxide and nitric oxide in dilute alkali are expressed in Equations I and II:

$$3NO_2 + 2NaOH = 2NaNO_3 + NO + H_2O \qquad (I)$$

$$NO + NO_2 + 2NaOH = 2NaNO_2 + H_2O \qquad (II)$$

$$2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O \qquad (III)$$

Equation III represents the direct sum of I and II, but is not indicative of the mechanism of absorption.

Dry mixtures of nitrogen oxides or mixtures containing water vapor not in excess of the saturation value of the corresponding nitric acid at the temperature of the absorption apparatus react strictly in accordance with the above equations. Thus a gas containing an equimolar or less proportion of NO_2 yields pure nitrite on absorption, the excess NO escaping from the solution as such. Mixtures containing an excess of NO_2 are completely absorbed in alkali, with the production of a mixture of nitrate and nitrite. The concentration of HNO_3 vapor in such a gas is in general negligible. It has been determined that HNO_3 and NO cannot coexist in a gas in appreciable quantities.

In the presence of nitric acid mist[5] or fog (as distinct from vapor) the absorption takes place as represented above. There is, however, an additional production of nitrate due to the simple absorption and removal of the mist by alkali.

The absorption of nitrous gases which contain relatively large quantities of water vapor and which are at an elevated temperature, such as obtains before a nitric oxide reaction chamber, is a somewhat more involved process than the simple cases above outlined.

As long as but one phase is present nitric acid vapor is practically nonexistent in a gas containing NO. However, as the temperature of such a gas falls in its passage to the

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[1] Received September 9, 1921.

[2] Published by permission of the Chief of Ordnance, War Department.

[3] Burdick and Freed, *J. Am. Chem. Soc.*, **43** (1921), 518.

[4] Results to be published later.

[5] This mist is not concentrated nitric acid, but is acid of that composition which is in equilibrium with the nitrous gases at the temperature in question. Thus, the mist entrained in a gas containing 0.5 per cent NO_2 and 0.7 per cent NO is a fog or suspension of droplets of 35 per cent nitric acid.[3]

absorption bottle, there is a condensation of fog or mist particles and the reaction

$$3NO_2 + H_2O\ (liq.) \rightleftharpoons 2HNO_3\ (aq.) + NO$$

takes place. Since this is not an oxidizing or reducing reaction, there is no change in the degree of oxidation of the mixture as a whole, but there is a radical change in its constitution and composition. It has changed from a gaseous mixture containing substantially nothing but NO_2, NO, water vapor, and diluent gas to a two-phase mixture containing aqueous nitric acid in the liquid phase as a mist, and NO_2, NO, and water vapor in the gaseous phase, the whole being practically at chemical equilibrium. It is the composition of this latter mixture which determines the absorption behavior in the presence of the alkali. For example, analysis of a gas mixture sampled from a main leading to a reaction chamber showed the composition of the gas reaching the alkali solution to be

	Per cent
HNO_3 mist	0.2[1]
NO_2	0.5
NO	0.7
TOTAL	1.4

[1] Expressed as percentage by volume HNO_3. It would be that volume occupied by the HNO_3 in the mist if it were vaporized without decomposition.

The mean degree of oxidation of this gas mixture in terms of NO_2 is 57 per cent. Actually at the temperature of the gas in the flue (80°) there was no mist existent. The composition of the gas was

	Per cent
NO_2	0.8
NO	0.6
TOTAL	1.4
Degree of oxidation	57.0

The total oxides and degree of oxidation are the same in both cases. The last analysis represents the composition of the warm gas at 80° flowing in the pipe, whereas the first represents the composition of the same gas after being cooled to 30°.

If the equations of absorption were accepted without consideration it would be anticipated that the warm gas in the pipe, since its degree of oxidation was over 50 per cent, would produce a mixture of nitrate and nitrite only and that NO would escape from the absorbing alkali solution. As a result of the condensation of mist on cooling and subsequent progress of the hydrolytic reaction, there was a considerable change in the composition of the gaseous phase of the mixture and, as a matter of fact, very nearly one-third of the NO originally present escaped absorption in the first alkali train in the absorption apparatus.

It is evident, then, that an analytical apparatus for the determination of the total oxides of nitrogen and their degree of oxidation which is to employ the principle of rapid absorption in alkali must consist of two parts, an alkali train for the absorption of all of the NO_2 and part of the NO and an aspirating flask or similar device in which the quantity of escaping NO may be determined.

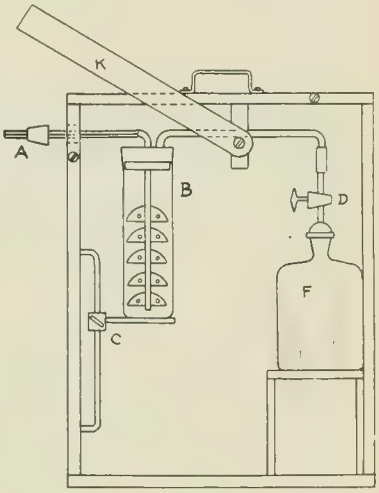
DESCRIPTION OF APPARATUS

A portable apparatus which has been found convenient for control purposes is shown in the figure. It consists of a frame supporting the absorption bulb B and the aspirating bottle F. The inlet tube A of capillary tubing is protected by the projecting strap iron or wooden guard K which may be raised out of position. The absorber in B is of the special form shown. It has the advantage of being a very efficient absorber, not requiring a large volume of solution, and not requiring a special containing flask. The clamp C is used as a support for the absorption apparatus. The absorption apparatus is connected to the evacuated aspirator bottle by a short rubber connection. The volume of the aspirator bottle should be known within 1 per cent.

PROCEDURE FOR ANALYSIS

A known amount of 0.1 *N* alkali (carbonate-free) is run into absorption bulb B and diluted with water until the liquid is at the top of the first bell. According to the concentration of the nitrous gases, from 10 to 50 cc. of carbonate-free alkali will be required. An automatic pipet may be conveniently used. The aspirator bottle must be evacuated and all connections and stoppers should fit firmly, so that absence of leaks is insured. With the strap iron or wooden guard K let down, the apparatus may be safely carried.

In sampling, the tube A is firmly seated in the opening in the flue and the measured quantity of gas aspirated slowly through. The rate of bubbling through the absorber may be a little faster than the bubbles at the base of the inlet tube can be counted. Cock D is then closed. The opening in the apparatus frame through which tube A projects is purposely made large so that a certain flexibility of setting is obtained. In withdrawing or introducing the sample tube it should be kept well centered in the pipe opening to avoid nitric acid running off the walls into the tube.



The solution is removed for analysis by lowering the bulb B and rinsing the absorber carefully with distilled water. The inside of the sample tube is also rinsed with water and the wash water added to the original solution, which is transferred to a beaker. In case it is necessary to employ an extension on the sample tube it too must be rinsed with water to remove any condensate.

The alkaline solution is titrated back with 0.1 *N* sulfuric acid, using a few drops of a solution of methyl red in dilute (0.01 *N*) alkali as an indicator. Alcoholic solutions must be avoided because of the later titration with permanganate. The solution from the alkali neutralization is transferred to the beaker used for the permanganate titration. Two beakers preferably are used in order to obviate any liability of transfer of strong acid from the permanganate titration to the alkali solutions subsequently to be analyzed. A few preliminary cc. of 0.1 *N* permanganate are added, and 5 cc. of concentrated sulfuric acid are stirred in, care being taken that the solution is maintained continuously of a pink color by running in permanganate. With the first drop or so of permanganate the pink color due to the methyl red indicator is destroyed. After an excess of permanganate has been added the solution should be allowed to stand for 2 or 3 min. in order that the relatively slow reaction of permanganate with the nitrite may complete itself. A slight excess of ferrous sulfate solution (whose relative strength in terms of the permanganate is known) is added and the solution is titrated with permanganate to a permanent pink. A blank determination of the amount of permanganate necessary to decolorize the methyl red indicator added should be made.

The oxides of nitrogen in the aspirator bottle are determined in the way customarily employed. Through the stopcock D are run successively 5 cc. hydrogen peroxide, 5 cc. water and, if necessary, approximately 10 cc. oxygen. The bottle is shaken and, after the oxides have largely been absorbed, an excess of 0.1 *N* alkali is added. The bottle is again shaken and allowed to stand until all oxides are absorbed. It is then rinsed out and the excess alkali titrated with standard acid.

COMPUTATION OF ANALYSIS AT POINT OF SAMPLING

Case 1—All Components Gaseous and No Mist Present

The equivalent cc. of alkali neutralized by the gas passed through the absorber and the gas in the aspirator bottle and the permanganate used are computed, and the calculations[6] made as follows:

A = Cc. 0.1 *N* alkali neutralized by nitrogen oxides in absorber.
P = Cc. 0.1 *N* permanganate used to oxidize nitrite in absorber.
C = $^1/_2$ (3A + P) = Cc. 0.1 *N* alkali neutralized by NO_2.
D = Total alkali − C = Cc. 0.1 *N* alkali neutralized by NO.
E = C/4 = Per cent by volume of NO_2 in gas.[7]
F = D/4 = Per cent by volume of NO in gas.
E + F = Total oxides present.

$$100 \times \frac{E}{E+F} = \text{Percentage oxidation of nitrous gases in terms of } NO_2.$$

The composition of the nitrous gases as above computed represents that which it would have were all components completely gasified. Such conditions obtain when the temperature of the gas at the point of sampling is above the dew point and no fog or mist exists.

A subsidiary case may be encountered occasionally when the gas consists entirely of HNO_3 and NO_2, NO being completely absent. If this be met with, the percentage oxidation is over 100 per cent. Under these conditions the components are determined by the relationships:

$$\text{Total } NO_2 = 2 \times \text{Total nitrite in Alkali I}$$

$$\text{Total } HNO_3 = \text{Alkali I} + \text{Alkali II} - \text{Total } NO_2$$

Case 2—Mist Present in Gas Line and Temperature of Gas at Point of Sampling Approximately That of Alkali Absorber
(NO in excess over NO_2)

From a consideration of Reactions II and III and the reaction

$$HNO_3 \text{ (mist)} + NaOH = NaNO_3 + H_2O$$

and bearing in mind that any excess NO will escape from the first alkali solution, the following identities may be written:

$$\begin{aligned}\text{Total } HNO_3 \text{ mist} &= \text{Nitrate present in Alkali I}\\ &= \text{Alkali I} - \text{Nitrite in I}\\ \text{Total } NO_2 &= \frac{\text{Nitrite in I}}{2}\\ \text{Total NO} &= \frac{\text{Nitrite in I}}{2} + \text{Alkali II}\end{aligned}$$

For 0.1 *N* solution these become

$$\begin{aligned}\text{Total } HNO_3 \text{ mist} &= \text{Alkali I} - \frac{\text{Permanganate}}{2}\\ \text{Total } NO_2 &= \frac{\text{Permanganate}}{4}\\ \text{Total NO} &= \frac{\text{Permanganate}}{4} + \text{Alkali II}\end{aligned}$$

The percentages by volume of the constituents are computed in the same way as for Case 1. The percentage oxidation is given by the expression:

$$\frac{\text{Per cent } HNO_3 \times 2.5 + \text{per cent } NO_2 \times 2 + \text{per cent NO}}{\text{Total percentage}} - 1$$

CORRECTION FOR OXIDATION IN TRANSIT

The composition of the gas as calculated represents that at the moment of reaching the alkali, and consequently for a mixture containing excess oxygen does not represent the composition in the pipe at the point of sampling but at a point somewhat further along the pipe. From a knowledge of the rate of oxidation of NO it is possible to compute the composition at any point along the pipe line provided the rates of flow are known. For dilute gas mixtures containing less than 5 per cent excess oxygen, a correction for the oxidation taking place in the sample tube and gas analysis apparatus is in general unnecessary. In case, however, the diluent gas is air, the correction must be made. The complete equation[4] for the rate of oxidation of NO is:

$$15\,t = \frac{1}{2C_0 - C_1}\left(\frac{1}{C} - \frac{1}{C_1}\right) - \frac{2.3}{(2C_0 - C_1)^2} \log\,(2C_0 - C_1 + C)\,\frac{C_1}{2C_0C}$$

where C_0 = Concentration of oxygen at time $t = 0$ (mol. fraction).
C_1 = Concentration of nitric oxide at time $t = 0$.
C = Concentration of nitric oxide at time $t = t$.

When oxygen in considerable excess is present the equation may be simplified into

$$\frac{1}{C} - \frac{1}{C_1} = 30(C_0)t,$$

which is quite accurate enough for calculating the correction term.

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[6] BASIS OF CALCULATION
NO_2 reacting according to Equation I = 3/2 Alkali I
NO_2 reacting according to Equation II = 1/2 nitrite
Total NO_2 = 3/2 Alkali I + 1/2 nitrite
NO = Alkali I + Alkali II − total NO_2
If 0.1 *N* solutions are used

$$\text{Total } NO_2 = 3/2 \text{ Alkali I} + \frac{\text{Permanganate titration}}{2} = \frac{3 \text{ Alkali titration} + \text{Permanganate titration}}{2}.$$

[7] The number of moles of nitrogen peroxide absorbed in alkali is equal to the number of equivalents of alkali neutralized by nitrogen peroxide, or $\frac{C}{10000}$.

The number of moles of inert gas in the aspirator bottle is calculated from the equation $pv = n$RT. The pressure (as a result of observation) has been found to average closely 1.5 cm. Hg vacuum (corresponding to the height of liquid in the absorption bulb). The pressure is, therefore, $\frac{745}{760} = 0.98$ atm. The volume is one liter and the temperature is, therefore, about 25° C., or 298° Abs. The number of moles of inert gas is then given by the solution $n = \frac{PV}{RT} = \frac{0.98 \times 1.0}{0.0821 \times 298} = 0.04$ mole.

The percentage of NO_2 is therefore $100 \times \frac{C}{10000 \times 0.04} = \frac{C}{4}$ and correspondingly the percentage of NO is found to be $\frac{D}{4}$. The variations in temperature and pressure which will be found in the gas in the aspirator bottle are not enough to influence appreciably the calculated percentages of NO_2 and NO. Of course, if the volume aspirated is other than one liter, the proper factor must be calculated. For a volume of 1.15 liters the factor is 4.6.

Cadmium in 1921

Figures obtained from producers by the United States Geological Survey show that the total production of metallic cadmium in 1921 was 65,101 lbs., a decrease of 64,182 lbs., or about 50 per cent, as compared with the production in 1920. On the other hand, the production of cadmium sulfide in 1921 amounted to 65,446 lbs., an increase of 33,313 lbs., or more than 100 per cent, over the production in 1920.

The value of the metallic cadmium produced was $63,799 and that of the cadmium sulfide was $71,336, making a total value of $135,135, as compared with $188,535 in 1920, a loss of 28 per cent. The average selling price of metallic cadmium in 1921 was 98 cents a pound, as against $1.17 in 1920, and that of cadmium sulfide was $1.09 a pound, as against $1.16 in 1920.

A noteworthy development of the year was the extension of the use of cadmium electroplating for preventing rust.

The University of West Virginia is having plans prepared for the erection of a new chemical laboratory, estimated to cost about $400,000.

The Electrolytic Preparation of Arsenate of Lead[1]

By Herman V. Tartar[2] and Gary G. Grant

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A mixture of the basic and acid arsenates of lead can be prepared electrolytically from disodium arsenate or arsenic acid. When disodium arsenate is used the product contains a large portion of the basic compound. If on the other hand, arsenic acid is used the product may be made to contain a large proportion of the acid compound.

The object of this investigation was a quantitative study of the process to ascertain what concentration of arsenic acid, current density, distance between electrodes, and kind and concentration of electrolyte served best for the formation of lead hydrogen arsenate; also the effect of the above factors on current efficiency, electrical energy efficiency, and freedom from accumulations on the anode. Since lead hydrogen arsenate is the chief component of the commercial insecticide, attention was not given to the production of the basic arsenate.

The conditions most suitable for the electrolysis involve a concentration of approximately 0.05 per cent arsenic acid, a current density of 1.25 to 1.875 amp. per sq. dm., and a distance between electrodes of 2.5 to 5.0 cm. The most desirable electrolyte is sodium chlorate at a concentration of 1 to 2 per cent. If the precipitate is allowed to stand for several days in contact with the 0.05 per cent arsenic acid the proportion of acid arsenate is increased. Current efficiencies are very good.

Because of the extensive use of the arsenates of lead for insecticidal purposes, a number of investigations have been made during recent years to ascertain their constitution and properties. The work of Tartar and Robinson,[3] Smith,[4] and McDonnell and Smith[5] has shown that the commercial material may contain two compounds: *viz.*, lead hydrogen arsenate ($PbHAsO_4$) and a basic arsenate [$Pb_4(PbOH)(AsO_4)_3H_2O$].

At first lead arsenate was prepared for commercial use by the reaction between lead acetate or lead nitrate and disodium arsenate. Several other methods have been proposed during recent years; in fact, some twenty-five patents have been granted covering various processes. So far as the writers are aware the most direct and possibly the most widely used procedure is that proposed by Luther and Volck,[6] in which lead oxide is suspended in a solution of arsenic acid with a small amount of nitric or acetic acid as a catalyzer; either the basic or the lead hydrogen arsenate is produced, depending on the relative quantities of lead oxide and arsenic acid used. The literature on the subject affords no reference to an electrolytic method for the preparation of lead arsenate.[7]

Nearly two years ago some qualitative tests made in this laboratory showed that a material similar to much that is sold on the market could be prepared electrolytically in a manner somewhat analogous to the Luckow process for white lead. The bath consisted of a solution of an electrolyte to form a soluble lead salt (sodium chlorate was used) and a second electrolyte to furnish the arsenate ion to precipitate the lead as insoluble lead arsenate. The electrolysis was made with lead electrodes.

Experimental Part

The apparatus consisted of rectangular glass jars 3 × 4 × 6 in. and electrodes of lead 2.5 in. wide which dipped into the electrolyte 2.5 in. A copper coulometer was used for measuring the quantity of electricity used and the current was controlled approximately by means of a resistance and an ammeter. The fall of potential in the bath was ascertained by a voltmeter which could be shunted between the electrodes. A mechanical stirrer was used in some cases to agitate the electrolyte. In later experiments compressed air was found to be suitable for stirring.

After each electrolysis was completed, the precipitate was allowed to settle, filtered on a Büchner funnel, dried at 115°, weighed, reduced to a powder in a mortar, and analyzed. The lead was determined as lead chromate[8] and the arsenic by reduction to arsenious acid and titration with standard iodine solution.[9] From the amount of lead in the precipitate and the quantity of copper deposited in the coulometer the current efficiency was calculated on the basis of Faraday's Law.

The arsenic acid used was prepared from arsenic oxide which was found to contain no other impurity than a small amount of arsenious oxide. This was removed by treating the material with a sufficient quantity of concentrated nitric acid and evaporating several times to dryness to remove the excess of the nitric acid. The arsenic acid obtained was made up to volume and standardized. In this form calculated amounts were added at regular intervals to the electrolysis bath in order to maintain a fairly constant acidity.

The sodium chlorate and sodium acetate employed were both guaranteed as C. P. by a reliable manufacturer.

Effect of Concentration of Arsenic Acid

Three solutions were made up containing 4 per cent sodium chlorate and three different concentrations of arsenic acid. They were electrolyzed between lead electrodes each having an effective area of 6.25 sq. in. with a current of 0.5 amp. The results are given in Table I.

Table I Effect of Concentration of Arsenic Acid

Bath number	1	2	3
Concentration arsenic acid (as As_2O_6), per cent	1	2	5
Phenomena at anode	White precipitate	Little precipitate	No precipitate
Phenomena at cathode	Some lead deposited	More lead deposited	Much lead deposited

Because of the evident lowering of current efficiency by the deposition of lead on the cathode, these electrolyses were abandoned after a short time. Too high acidity causes the retention of lead in solution and it is deposited on the cathode during electrolysis. While lead is above hydrogen in the electromotive series it is easily deposited under these conditions because of the high overvoltage of hydrogen on lead electrodes. The presence of lead in the solutions was shown by making them alkaline with ammonia, which

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[1] Received September 29, 1921.

[2] Associate Professor of Chemistry

[3] *J. Am. Chem. Soc.*, **36** (1914), 1843.

[4] *Ibid.*, **38** (1916), 2014.

[5] *Ibid.*, **38** (1916), 2027; **39** (1917), 937.

[6] U. S. Patent 892,603.

[7] The reviewers of this paper have called the authors' attention to the method proposed in U. S. Patent 870,915 in which the anodic processes are very similar. The method proposed here is, however, more simple, and data are given regarding current efficiency, the proper composition of the bath, the amount of electrical energy required, and the composition of the lead arsenate obtained.

[8] Methods of Analysis of Official Agric. Chemists, **1920**, 57.

[9] *Ibid.*, 58.

permits the precipitation of basic lead arsenate;[3] the amounts present corresponded to the relative acidity of the baths.

Three more baths were electrolyzed in the manner stated above. Their composition and the results of the electrolyses and analyses are given in Table II.

TABLE II—FURTHER RESULTS ON EFFECT OF CONCENTRATION OF ARSENIC ACID

Bath number	4	5	6
Concentration of As_2O_5, per cent	0.5	1.0	1.0
Concentration of HNO_3, per cent	. .	1.0	. . .
Concentration of Na_2HAsO_4, per cent	. . .	. . .	1.0
Concentration of $NaClO_3$, per cent	4.0	4.0	4.0
Phenomena at anode	Flocculent lead arsenate	Same, but crystalline	Slimy lead arsenate
Phenomena at cathode	Some lead deposited	Much lead deposited	No lead deposited
Yield, grams	14.9	Small	12.5
Per cent lead	60.4	59.67	64.82
Current efficiency, per cent	91.0	Small	82.5
Theoretical per cent lead in $PbHAsO_4$	59.69		
Theoretical per cent lead in $Pb_4(PbOH)(AsO_4)_3H_2O$	69.6		

Pure crystalline lead hydrogen arsenate can be prepared by using nitric acid, but the current efficiency is very low. The use of disodium hydrogen arsenate to repress the ionization of the arsenic acid and increase the concentration of arsenate ion results in a lower current efficiency, and the product is more basic than with arsenic acid as the sole source of the arsenate ion.

More dilute solutions of arsenic acid were next tried. Iron cathodes were used for these experiments and were found satisfactory; by their use the hydrogen overvoltage is materially lowered. The results are tabulated in Table III.

TABLE III—FURTHER RESULTS ON EFFECT OF CONCENTRATION OF ARSENIC ACID

Bath number	7	8
Concentration of $NaClO_3$, per cent	4	4
Concentration of As_2O_5, per cent	0.25	0.05
Current density, amp./dm.^{2}	1.24	1.24
Phenomena at anode	Finely divided lead arsenate	Precipitate more finely divided
Phenomena at cathode	Some lead	Almost no lead
Yield, grams	Not continued	6.55
Per cent lead	. . .	61.66
Current efficiency, per cent	. . .	99.5

The results show that lead arsenate (a mixture of lead hydrogen arsenate and the basic arsenate, the former predominating) is produced without appreciable deposition of lead at the cathode if the concentration of arsenic acid is kept low enough and nearly constant during the electrolysis. The product is quite finely divided and on drying gives a very fine powder.

EFFECT OF CURRENT DENSITY

Two electrolyses were made in the same manner as that reported for Bath 8, except that current densities were 0.625 and 1.875 amp. per sq. dm., respectively. The data are recorded in Table IV.

TABLE IV—EFFECT OF CURRENT DENSITY

Bath number	9	10
Concentration of As_2O_5, per cent	0.05	0.05
Concentration of $NaClO_3$, per cent	4.0	4.0
Current density, amps./dm.^{2}	0.625	1.87
Voltage with 2.5-cm. distance between electrodes	1.0	2.0
Voltage with 10-cm. distance between electrodes	3.0	6.0
Yield, grams	9.65	9.5
Time (approximately), hours	6	2
Per cent lead	62.4	62.05
Current efficiency, per cent	98.8	99.6

The higher current density apparently favors the formation of the acid compound and gives at the same time a higher current efficiency. The precipitate also has less tendency to stick to the anode. Considering the voltage drop across the baths, however, the actual energy efficiency is less with the higher current density. This may be offset to some extent by placing the electrodes closer together.

EFFECT OF ELECTRODE DISTANCE AND VOLTAGE

These experiments were carried out to ascertain the effect of distance between electrodes on the voltage drop across the bath, the composition of the precipitate, and the deposition of lead at the cathode. The data are given in Table V.

TABLE V—EFFECT OF ELECTRODE DISTANCE ON VOLTAGE

Bath number	11	12	13
Electrode distance, cm.	10	5	2.5
Concentration of As_2O_5, per cent	0.05	0.05	0.05
Concentration of $NaClO_3$, per cent	4.0	4.0	4.0
Voltage	4	2	1
Current density, amps./dm.^{2}	1.24	1.24	1.24
Yield, grams	9.226	9.24	9.48
Per cent lead	65.05	63.7	62.5
Current efficiency, per cent	99.5	97.6	98.3
Character of precipitate	Most dense	Medium dense	Most finely divided

The formation of lead hydrogen arsenate is favored, greater energy efficiency is realized, and less lead is deposited at the cathode with the electrodes close together. The difference in the physical character of the precipitates was striking. The one from Bath 13 slid off the electrode quite freely and in a finely divided state suitable for use as insecticide material.

USE OF DISODIUM HYDROGEN ARSENATE AND OF SODIUM ACETATE IN ELECTROLYSIS BATH

An attempt was made to use a bath containing disodium hydrogen arsenate and acidified with arsenic acid solution so that the hydrogen-ion concentration was approximately that of 0.05 per cent arsenic acid solution. Under these conditions the acidity could be more easily controlled and kept more nearly constant. The bath was 4 per cent sodium chlorate and 1 per cent disodium hydrogen arsenate, made acid to methyl orange, thus giving a solution of approximately the composition NaH_2AsO_4. The electrolysis gave a dense precipitate which adhered strongly to the electrode; the formation of oxides of lead also occurred at the anode. The current efficiency was obviously low and the run was stopped after a short time. The writers have no complete explanation to offer for the anodic phenomena observed.

A bath containing sodium acetate instead of sodium chlorate was found to give good results in many respects. Much less lead was deposited at the cathode using even a 1 per cent arsenic acid. It was found, however, that higher concentrations of sodium acetate were necessary than of sodium chlorate. Some of the results are tabulated in Table VI.

TABLE VI—RESULTS OBTAINED WITH SODIUM ACETATE IN ELECTROLYSIS BATH

Bath number	14	15
Concentration of $NaC_2H_3O_2$, per cent	5	8
Concentration of As_2O_5, per cent	1	1
Current density, amps./dm.^{2}	1.25	1.25
Electrode distance, cm.	10	10
Voltage	4.0	3.0
Yield, grams	9.25	17.3
Per cent lead	63.8	63.7
Current efficiency, per cent	98.6	98.7

A very uniform product can be obtained by this method. The lead arsenate formed is more basic and less finely divided than that secured from the chlorate bath.

EFFECT OF CONCENTRATION OF SODIUM CHLORATE

Qualitative experiments indicated that the concentration of this substance might affect the physical properties of the precipitate and its tendency to stick to the electrode. Three baths were tried containing concentrations of sodium chlorate above and below those used in previous experiments. These were electrolyzed under similar conditions and the data are reported in Table VII.

The more dilute solutions of sodium chlorate favor the formation of the acid arsenate. In these cases practically

TABLE VII—EFFECT OF VARIATION OF CONCENTRATION OF SODIUM CHLORATE IN ELECTROLYSIS BATH

Bath number	16	17	18
Concentration of $NaClO_3$, per cent	4	2	1
Concentration of As_2O_5, per cent	0.05	0.05	0.05
Current density, amps./dm.^{2}	1.25	1.25	1.25
Phenomena	Little lead at cathode	No lead	No lead
Character of precipitate	Least finely divided	Finely divided	More finely divided
Voltage	4	4	4
Distance between electrodes, cm.	8.5	5.5	3
Yield, grams	5.926	6.32	6.371
Per cent lead	65.6	60.95	60.4
Current efficiency, per cent	98.3	97.4	97.2

no lead was deposited at the cathode, although the acidity was allowed to run up as high as 0.2 per cent at times. It was also observed that violent stirring of the electrolyte caused the precipitate to cake on the electrode, while as long as the bath was allowed to remain quiet it formed in flakes and fell freely to the bottom of the tank. If, however, the electrolyte was not circulated to some extent, the concentration of arsenic acid became depleted between the electrodes, the bath became alkaline to phenolphthalein at this point, and lead was deposited at the cathode. To obtain a slow circulation of the electrolyte, air was slowly bubbled in at one corner of the tank.

The results presented above indicate that the best conditions are as follows:

Concentration of sodium chlorate, per cent	1 to 2
Concentration of arsenic acid, per cent	0.05
Current density, amp./dm.^{2}	1.875
Distance between electrodes, cm.	2.5 to 5.0
Electrolyte slowly circulated.	

In order to confirm the above results three baths were made up of the above concentrations and run according to the best conditions as determined in the preceding experiments. The results are tabulated in Table VIII.

TABLE VIII—RESULTS OF ELECTROLYSES WITH BEST CONDITIONS FOUND

Bath number	20	21	22
Concentration $NaClO_3$, per cent	2	2	2
Concentration As_2O_5, per cent	0.05	0.05	0.05
Current density, amps./dm.^{2}	1.875	1.875	1.875
Electrode distance, cm.	2.5	2.5	2.5
Voltage	3.0	3.0	3.0
Yield, grams	6.4038	6.3946	6.3655
Per cent lead	61.9	61.85	62.55
Current efficiency, per cent	98.6	98.4	98.9
Gain on coulometer cathode, grams			1.2374
Total coulombs			3760
Time (sec)			4800
Average current, amp.			0.784
Kw. hrs. used			0.00313
Kw. hrs. per lb. lead arsenate			0.222

In addition to the above experiments and in order to determine the effect of allowing the precipitate to stand in contact with the electrolyte the following experiment was conducted: A sample of lead arsenate from Run 11 containing 65.05 per cent lead was placed in a 0.05 per cent arsenic acid solution and shaken up at intervals for 5 days. It was then filtered off and analyzed for lead, when it was found to be 59.4 per cent lead (very near to the theory for lead hydrogen arsenate). This would indicate that by allowing the precipitate to stand for several days in contact with the bath solutions a product could be obtained containing practically pure lead hydrogen arsenate.

The Physical Properties of Commercial Arsenates of Lead[1]

By **R. H. Robinson**[2]

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Chemical analysis shows very little variation in the brands of lead arsenate now on the market. Work on twelve commercial brands, which forms the basis of the following paper, shows marked differences in certain physical properties which may affect the efficiency of the spray.

Specific gravity varies only slightly, and there is apparently no correlation between this value and dry volume. Appreciable differences are observed in the size of particles, in the proportion of large to small particles, and in suspension qualities.

In order to give lead arsenate better spreading properties, it is the custom of orchardmen to add spreaders such as soap solution, oil emulsions, etc. These cannot be used under all climatic conditions, and several commercial arsenates contain harmless organic substances as "deflocculents." Their function is chiefly to penetrate and subdivide the clusters of fine particles of arsenate, causing them to remain in suspension for a long time and increasing their spreading properties and also, probably, their adhering properties. In the course of the experiments herein reported similar deflocculating properties were produced in other commercial arsenates by the addition of small amounts of calcium caseinate, glue, soap solution, tannin, certain sugars, gum arabic, oil emulsions, and dextrin.

The amount of lead arsenate, which will remain in suspension in water for a specified length of time, is perhaps the best indication of its efficiency. The practical efficiency of any deflocculent which may be added to a commercial lead arsenate can best be determined by results obtained in field practice, where only ordinary care is exercised in the application of the spray.

SINCE the time that arsenicals were first employed as insecticides in the control of the codling moth, chemical investigations have been carried on in order to learn definitely regarding the composition of the various arsenates of lead and to choose those forms which will be most efficient. A desirable commercial product must be high in total arsenic for optimum killing efficiency, low in water-soluble arsenic in order that foliage burn may not occur, and free from foreign impurities. Investigations to this end have been successful and two forms of lead arsenate are now on the market, namely, the acid or hydrogen arsenate and the "neutral" or basic arsenate. It has been found by experimentation that the killing efficiency of the former is superior to the latter; consequently more than 95 per cent of the lead arsenate on the market is the lead hydrogen arsenate form.

Chemical analyses of samples of lead arsenate submitted to the chemical department of the Oregon Experiment Station during the past several years have shown that manufacturers are producing a very high-grade product, free from impurities, and low in water-soluble arsenic. Representative samples were analyzed in 1920. Table I gives the results obtained.

The composition of the arsenates indicates only a slight variation between the different brands. Furthermore, this variation is not due to the presence of impurities. All the samples reported are of the lead hydrogen arsenate form, containing small amounts of the neutral lead arsenate, which accounts mainly for the slight variation in composition of the different brands. The low water-soluble arsenic content

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[1] Received September 3, 1921.

[2] Associate Chemist, Oregon Agricultural Experiment Station.

TABLE I—ANALYSES OF COMMERCIAL BRANDS OF LEAD ARSENATE

BRAND	Total PbO	Total As_2O_5	Water-Soluble As_2O_5
A	63.82	31.80	0.06
B	63.96	32.53	Trace
C	63.19	31.64	0.04
D	64.14	32.19	Trace
E	64.41	31.27	0.06
F	63.87	32.36	Trace
G	65.71	30.46	Trace
H	64.86	30.75	0.12
I	63.93	32.07	0.17
J	63.74	32.94	0.07
K	64.41	31.84	Trace
L	63.74	31.04	0.16

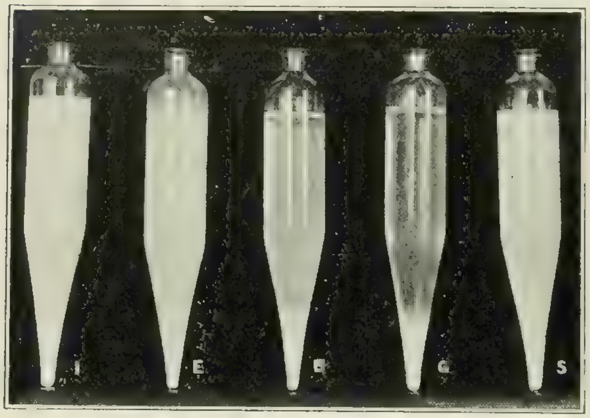


FIG. 1—NATURAL SETTLING PROPERTIES OF SOME COMMERCIAL LEAD ARSENATES

of all samples further emphasizes the high degree of purity of the commercial brands that are now found on the market. We can conclude, therefore, from these and numerous other analyses, that from the standpoint of their chemical composition all brands of lead arsenate are safe to use and equally efficient results are to be expected from any of them.

Any apparent differences in brands of lead arsenate now on the market may, therefore, be ascribed to their physical properties. A high-grade arsenical that will give best control of insect pests should not only contain a certain proportion of arsenic, but should also be in a very fine state of subdivision so that it will remain suspended in water for a reasonable length of time and, when sprayed, will adhere well and form a thin, uniform film of the poison on the surface to be covered. Superficial examination of the various commercial brands indicates that they differ widely in their physical properties. Some are finely ground, fluffy and bulky; others are coarse-grained and compact. Again we find some brands which contain a fraction of a per cent of an organic substance which tends to hold the arsenate suspended in water for a long period of time. For the sake of convenience, we shall refer to this substance as a "deflocculent" or "spreader," since it functions chiefly by causing deflocculation of the particles when suspended in water and manufacturers claim that better spreading of the arsenical is obtained when this material is added. The efficiency of the spray material is no doubt enhanced by the addition of a deflocculent, provided it adheres better and causes the drops of spray to flatten out and spread over a greater area.

In order to ascertain whether these differences are of such magnitude that one brand may be classified as superior to another, a study has been made of the physical properties of twelve brands collected in the market in 1920.

SPECIFIC GRAVITY AND DRY VOLUME

The specific gravity of a commercial lead arsenate may reflect a favorable or an unfavorable physical condition for spraying purposes. It was determined by ascertaining the weight of toluene displaced by a known quantity of the lead arsenate. Care was taken to remove occluded air by placing the pycnometer in an exhausted desiccator.

It has been observed that some brands of lead arsenate are light and fluffy and occupy a comparatively large volume, while others are compact and granular. To correlate the apparent dry volume with other data, gram portions were weighed out and transferred to graduated oil tubes of the type shown in Fig. 1. As the lower part of these tubes taper, the volume occupied may be read accurately to 0.1 cc. The tubes were tapped gently until the arsenates ceased to settle and the volumes recorded.

Table II gives the specific gravity at 20° C. referred to water at 4° C. and the dry volume for the twelve brands under observation.

TABLE II—SPECIFIC GRAVITY OF COMMERCIAL BRANDS OF LEAD ARSENATE

BRAND	Specific Gravity at 20°/4°	Dry Volume Cc. per Gram
A	5.69	4.3
B	5.87	2.5
C	5.69	1.9
D	5.91	3.4
E	5.82	2.6
F	5.88	3.0
G	6.01	3.2
H	5.91	3.4
I	5.62	1.8
J	5.80	2.5
K	5.91	1.9
L	5.84	2.3

The above results indicate only slight differences in the specific gravity of the various commercial lead arsenates. Apparently there is no correlation between the specific gravity and the dry volume. Some brands occupy more than twice the dry volume of certain other brands.

SETTLING TESTS

The length of time an arsenical will remain suspended in water is an indication to a limited extent of the size of the integral particles. The larger granules will settle immediately while the fine, flour-like particles will remain suspended in water for a longer period of time. A lead arsenate containing fine, flour-like particles is, of course, more desirable. In order to judge clearly between brands, distinction must be made between a lead arsenate that consists mainly of very fine particles and one that contains a high percentage of coarse particles together with a small amount of very fine particles that will remain in suspension a long time and render invisible the larger particles that settle immediately.

To determine the relative amounts of fine particles of the various commercial brands of lead arsenates which remained in suspension during a definite length of time, oil tubes containing 100 cc. of water and 1 g. of the lead arsenate were prepared. The tubes were agitated thoroughly and photographs were taken after settling for 5 min. Since all the brands which contained deflocculents were similar and those which did not contain deflocculents were also similar, only one photograph of a few of the contrasting brands is reproduced in Fig. 1.

It will be observed that Brands I and E, which contained deflocculents, remained in suspension while B and G settled. The photographs (not reproduced here) of Brands A, C, D, H, J, and K were similar to B and G. Brands F and L (not reproduced here), both of which contain deflocculents, were similar to E and I.

Chemical tests showed that those brands which remain in suspension for a long period of time contained deflocculents. These deflocculents were identified in three of the brands and were found to be harmless as an ingredient of a spray material. Since these deflocculents seem to penetrate the lead arsenate aggregates and cause them to subdivide instead of clinging together in clusters that settle rapidly, certain physical properties are no doubt improved by the addition of such materials.

The oil tube marked S in Fig. 1 exemplifies similar suspension and deflocculating characteristics that may be produced in any commercial arsenate by the addition of certain substances. This oil tube contains Brand G in water suspension, together with a small amount of calcium caseinate added as a deflocculent. Laboratory experiments show that calcium caseinate, glue, soap solution, tannin, certain sugars, gum arabic, oil emulsions, and dextrin act as deflocculents when used in certain amounts and probably are as good as those added to the four commercial brands. However, it is impractical for the consumer to use some of them, and others react chemically with lead arsenate and would cause burning of foliage; hence, it is not advisable to recommend definitely at this time how they may be employed.

Fig. 1 and the photographs of the other brands not reproduced here do not show some particular points that are distinctive of each brand. A low percentage of very fine particles may remain in suspension and tend to obscure the actual physical condition. Close examination during the settling process warrants the following remarks regarding the samples under observation: The small particles of Brands E and I, which contain deflocculents, were held in suspension while the larger granules settled. The former had a much higher percentage of the coarse particles than the latter. Brands A, C, and D contained a low percentage of coarse particles, the relative amounts increasing in the order named. Brand B was very uniform and finely subdivided; none of the larger granules that were plainly visible in most of the other brands could be detected. Brand G was peculiar in that it contained a comparatively high percentage of very coarse sand-like granules while it also showed a large amount of very fine flour-like particles. Brands K and L showed a very high percentage of coarse particles, although the latter contained a deflocculent that held the smaller particles in suspension. Brands F, H, and J contained a medium amount of coarse granules, while the remainder apparently were fine and uniform in size.

The photographs show that one brand of lead arsenate will remain in suspension in water longer than another, but only the approximate amount can be judged. In order to show the actual amounts that remain in suspension after 5 min., two methods were employed:

I—The glass tubes shown in the photograph, containing 1 g. of the arsenate and 100 cc. of water, were thoroughly shaken and allowed to stand 5 min. The particles which remained in suspension were siphoned off with the supernatant liquid, evaporated to dryness at 100° C., and weighed. The amount that settled was calculated by difference.

II—The other method was more rapid but not so accurate. A 1-g. sample was introduced into the graduated oil tube containing 100 cc. of water. After shaking thoroughly the tube was centrifuged for 1 min. at 1200 r. p. m. and the volume of the settled arsenate was noted. The tube was again shaken, allowed to stand 5 min., and the supernatant liquid and particles in suspension siphoned off. The tube was again centrifuged and a second reading taken of the settled arsenate. From the two readings the percentages of lead arsenate which settled and remained in suspension were calculated. Table III gives the results obtained for the twelve brands.

The results indicate a perceptible difference in the various brands of lead arsenate. Since only the very fine particles remain in suspension, the percentages reflect to a certain extent the relative amounts of large and small particles. The four brands containing a deflocculent naturally show the highest amounts that remain in suspension. The other brands did not vary greatly in the amounts that settled and remained in suspension. It is interesting to note that Brand G, which showed in the settling tests the presence of a larger amount of coarse, granular particles than any other brand, also contained a high percentage of the smaller particles that remained in suspension.

TABLE III—SETTLING TESTS ON LEAD ARSENATE

	METHOD I		METHOD II	
BRAND	In Suspension	Settled	In Suspension	Settled
A	1.78	98.22	2.4	97.6
B	3.63	96.37	4.2	95.8
C	1.84	98.16	2.2	97.8
D	2.50	97.50	1.7	98.3
E	90.75	9.25	90.2	9.8
F	71.62	28.38	71.5	28.5
G	8.96	91.04	9.6	90.4
H	4.85	95.15	5.0	95.0
I	76.60	23.40	72.2	27.8
J	2.64	97.36	1.7	98.3
K	2.85	97.15	2.6	97.4
L	12.84	87.16	12.7	87.3

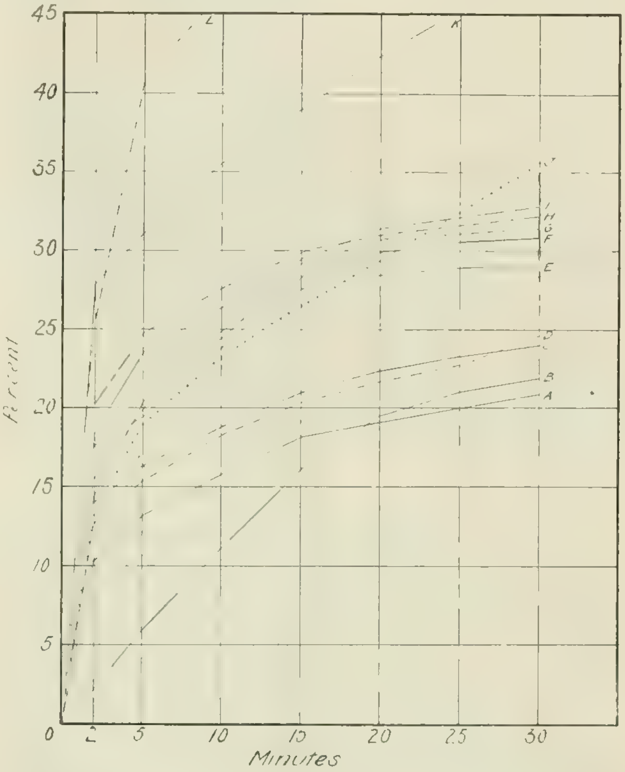


FIG. 2 PERCENTAGES OF PARTICLES OF COMMERCIAL LEAD ARSENATE SETTLING AFTER DEFLOCCULATION WITH GUM ARABIC

COMPARATIVE SIZE OF PARTICLES

The foregoing work does not give a true indication of the comparative size of the particles in the various commercial brands of lead arsenate because the presence of a deflocculating agent in some of the brands functioned by further subdividing the clusters of fine particles when added to water. In order to compare all brands on the same basis an attempt was made to find some organic substance which would act as a deflocculating agent for all brands alike and yet not cause precipitation of particles in those brands which contained a deflocculent that had been added by the manufacturer. After experiments with several substances gum arabic proved satisfactory. The graduated oil tubes were filled to the 100-cc. mark with a 0.2 per cent solution of gum arabic and 1-g. portions of the different brands were added to separate tubes. After occasional shaking during 2 hrs., the small particles were completely deflocculated, and the larger ones remained unchanged. Settling tests of the different brands were then made. At stated intervals readings were taken of the amount that settled, and finally the percentages which had settled in a given time were calculated.

Curves plotted from the percentages which settled in the time specified are shown in Fig. 2.

All of the curves except the one for Brand B indicate a rapid settling during the first 2 min., after which it becomes slower. This is due to the coarse granules, which are not affected by the deflocculating substance. The amount of these coarse particles also indicates that portion of the lead arsenate that probably is not of much benefit as a spray, since large granules will not adhere and are washed off easily by the rain. Specific points regarding the size of particles are as follows: The curve for Brand B indicates that this arsenate was the most uniform and contained the least amount of coarse particles. The curves for Brands A, C, and D showed that these brands contained about 12, 13.5, and 15 per cent, respectively, of large granules and were similar in general physical characteristics. Brands E, F, G, H, I, and J contained between 15 and 20 per cent of large granules. Brand G was especially noticeable, because part of the large granules were very coarse and sand-like in structure; Brand H also contained a smaller amount of similar size. As indicated by the curves, Brands K and L were abnormal. While they did not contain a greater amount of very coarse granules than the average brand, a high percentage of all particles was so large that they were not acted upon by the deflocculating agent and consequently settled quickly. This indicates an undesirable physical condition. These two brands contained also a medium amount of very fine particles which did not settle in 24 hrs.

Microphotographs of Lead Arsenate Particles

In order to gain further information regarding the size of the particles of different brands of lead arsenate and to distinguish between their spreading properties, microphotographs were taken of drops of the spray which had been transferred to clean slides and dried at room temperature. All slides were prepared by shaking 100 cc. of water containing 1 g. of the lead arsenate and removing a small drop by means of a capillary glass tube. The white sections in the photographs (Fig. 3) are the lead arsenate particles.

Photographs of all the different brands are not reproduced here on account of the great similarity between many of them. It will be observed from the prints that the main contrasting differences were between those brands containing deflocculents (Brands E and I) and those without the deflocculents (Brands C and B). Apparently brands containing a deflocculating agent are superior to the others since the particles seem smaller, uniform in size, and tend to form an ideal film. Brands without spreaders, on the other hand, seem to be grouped in somewhat irregular clusters with interstices between the groups of particles, or to run unevenly to one side to form a thick mass, as indicated by B. It is probable that the latter would be washed off quickly by the continued action of rain and heavy dew, while brands containing a deflocculating agent would offer less resistance and consequently tend to adhere longer to the surface covered.

Discussion

Of the differences in the physical properties of commercial brands of lead arsenate that may affect the efficiency of the spray, the size of the particles and their power to spread is perhaps of most importance. All brands contain, apparently, 80 per cent or more of fine flour-like particles that would be effective either as a dust spray or in water medium. These fine particles do not, however, spread over the surface as well as is desired and consequently spreaders, such as soap solution, oil emulsions, and other substances, are used by orchardmen in some sections of the country to augment the spreading properties. Under some climatic conditions, however, these spreaders cannot be used owing to reaction with the lead arsenate in which soluble arsenic is formed, which subsequently causes burning of foliage. The need, therefore, of an efficient, harmless spreader for lead arsenate is recognized. In four of the commercial brands studied, organic substances, or "deflocculating agents," have been incorporated in the lead arsenate during the manufacturing process. These materials are harmless and function chiefly by penetrating the clusters of very fine particles, causing them to deflocculate and, aided by the soluble deflocculent, to remain in suspension in water for a long time. Subdivision of clusters of fine particles or deflocculation obviously would increase the spreading properties. It would likewise probably increase the adhering properties since a smooth, even coating is made instead of thick spots scattered over the sprayed surface. On the other hand, a deflocculating agent, or a spreader, would be of no benefit if the particles were large and granular, as exemplified by Brand L.

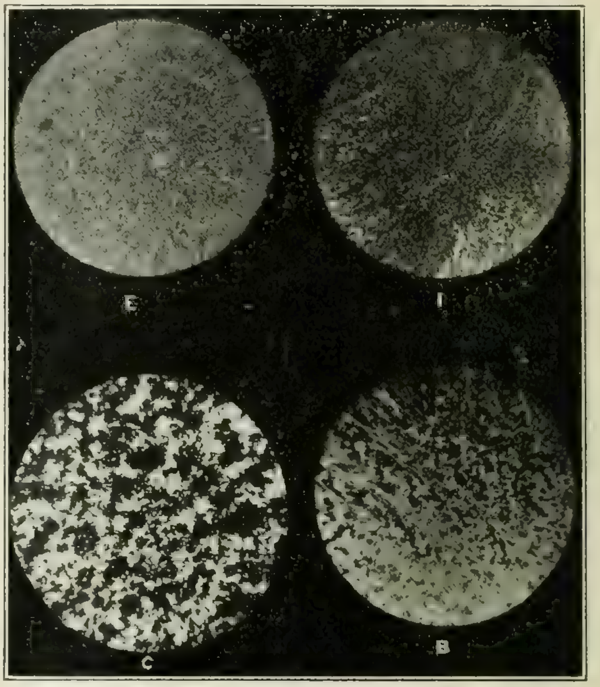


Fig. 3—Microphotographs of Particles of Commercial Lead Arsenates
(Approx. 15 Diameters)

It may be claimed that from 90 to 100 per cent control has been obtained with ordinary lead arsenate and consequently no further benefit would be derived from the addition of a deflocculating agent or spreader. This is no doubt true, especially in experimental work carried on at State Experiment Stations, where utmost care is used by an expert in the applications of the spray and where efficient high-powered spray outfits are employed. On the other hand, in most of our commercial orchards, careless manipulation, combined with faulty or indifferent application of spray material has to be contended with. In the latter case the addition of an efficient deflocculating agent or spreader would minimize poor results.

The physical properties of an arsenate of lead should be optimum to obtain maximum spreading and adherence of the spray material by the addition of an efficient deflocculent. The amount of lead arsenate that will remain in suspension in water for a specified length of time is perhaps the best indication of its efficiency. If most of the particles of a lead arsenate containing a deflocculent settle immediately while there is just sufficient in suspension to obscure its real physical condition, such an arsenate will not be as efficient as another with better physical properties and having no spreader. The practical efficiency of any deflocculent or spreader that may be added to a commercial lead arsenate can best be determined by comparison of results obtained in field practice where ordinary care only is exercised in the application of the spray.

Naphthalenesulfonic Acids[1,2]

IV—Solubilities of Some Amino Salts of Naphthalenesulfonic Acids

By H. Wales[3]

Color Investigation Laboratory, Bureau of Chemistry, Washington, D. C.

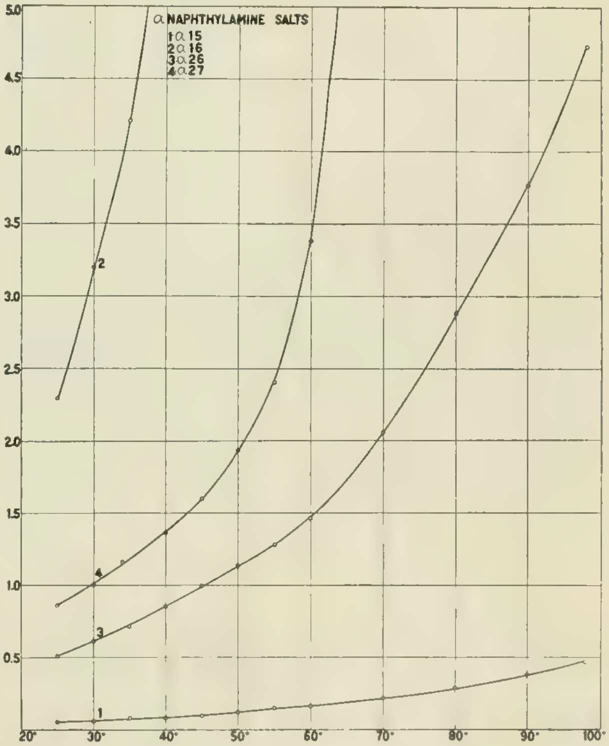
In the following paper the solubilities of the salts α- and β-naphthylamine with some naphthalenesulfonic acids have been determined between 25° and 98° C. and the results plotted. Allotropic changes are indicated for two of the salts and an interesting relation between the solubility and structure of a series of isomers is shown.

THE method of Ambler and Wherry[4] for the separation and identification of the sulfonic acids of naphthalene depends upon the formation of insoluble salts with α- and β-naphthylamine. With the exception of their solubilities, which were noted in only a general way, all properties of these salts have been thoroughly described.[5] Inasmuch as their complete separation depends upon the solubility, it was thought advisable to determine this over a wide range of temperatures.

METHOD

An excess of the salt was placed in a thermostat with the solvent and stirred at constant temperature for one day. At the end of this period a weighed amount of solution was drawn off through a pipet having a cotton plug over the end, evaporated to dryness, and the residue weighed. No difficulty caused by crystallization in the pipet was experienced at high temperatures for the reason that all the salts used form highly supersaturated solutions. Pure water proved to be impossible for use as a solvent, because of the rapid hydrolysis of the more soluble compounds. However, a 0.01 *N* solution of hydrochloric acid was sufficient to prevent hydrolysis except in the case of α-naphthylamine naphthalene-1,6-disulfonate. No effect of acid of this strength on the solubility could be determined, and the solvent has the added advantage of more nearly giving the conditions under which the salts are prepared[4] and used in detecting the sulfonic acids.

In the case of α-naphthylamine naphthalene-1,6-disulfonate, the rapid hydrolysis of this salt made a slightly different method necessary. The solvent, heated to a temperature 15° to 20° higher than that desired, was placed in a Dewar bulb with more than enough salt for saturation at this higher temperature. The liquid was then allowed to cool slowly with rapid stirring. When the desired temperature was reached, after 2 or 3 hrs., a portion was drawn off through a plugged pipet and treated as above. Freshly prepared samples were used in all these determinations since it was found that on standing for several months changes took place which seriously affected the solubility. For example, α-naphthylamine naphthalene-α-sulfonate and α-naphthylamine naphthalene-1,6-disulfonate showed much lower solubilities while the α-β, and α-1,5-compounds became almost twice as soluble. The nature of this change is not understood at this time. No change in this new compound could be brought about by recrystallization.



Considerable difficulty was experienced with solutions of α-naphthylamine naphthalene-2,7-disulfonate above 70° C. and with all solutions of α-1,6, since on partial evaporation on the steam bath these solutions would set to solid masses from which the last traces of water could be removed only by prolonged heating.

RESULTS

The results, calculated to grams of salt in 100 g. of solvent, are given in the accompanying table. When plotted, these results give the curves shown in the charts.

An interesting relation between the structure of a series of isomers and their solubilities is apparent from these results. From the very meager information available on the solubilities of isomers it was noted that the para or most

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[1] Received November 28, 1921.

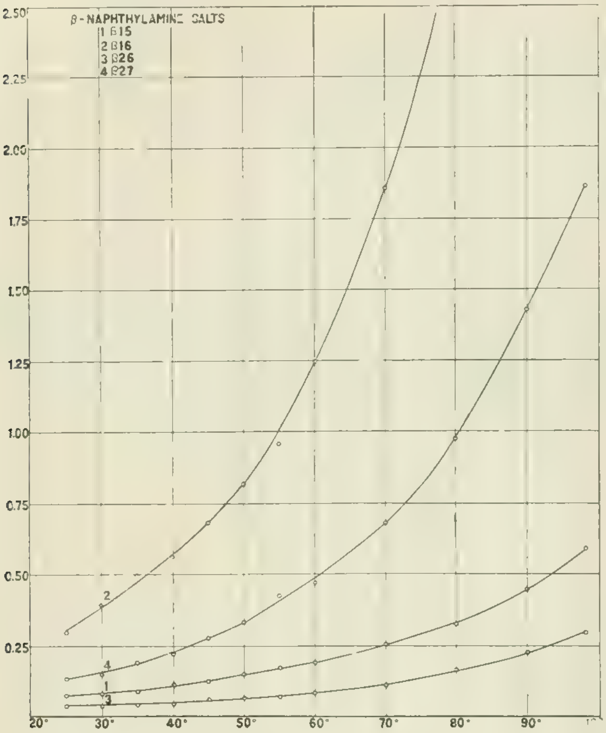
[2] Published as Contribution 56, from the Color Investigation Laboratory, U. S. Bureau of Chemistry, Washington, D. C.

[3] Associate Chemist (Physical).

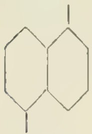
[4] THIS JOURNAL, **12** (1920), 1085.

[5] Ambler, *Ibid.*, **12** (1920), 1081, 1194.

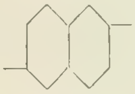
symmetrical isomer is the least soluble,[6] and that the order of solubility of the ortho and meta compounds varies according to the solvent. In general, the order is *o-m-p* for water and *m-o-p* for all other solvents except alcohol. For alcohol both arrangements are found.



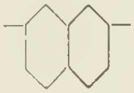
In the case of these compounds which are salts of disulfonic acids, the order of solubility, starting with the most soluble, is: *epi-* 1,6; *pros-*, 2,7; *amphi-*, 2,6; *ana-*, 1,5 for the α-naphthylamine salts; and *epi-*, 1,6; *pros-*, 2,7; *ana-*, 1,5; *amphi-*, 2,6 for the β-naphthylamine salts. The formulas



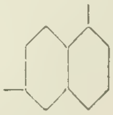
1,5
Ana-



2,6
Amphi-



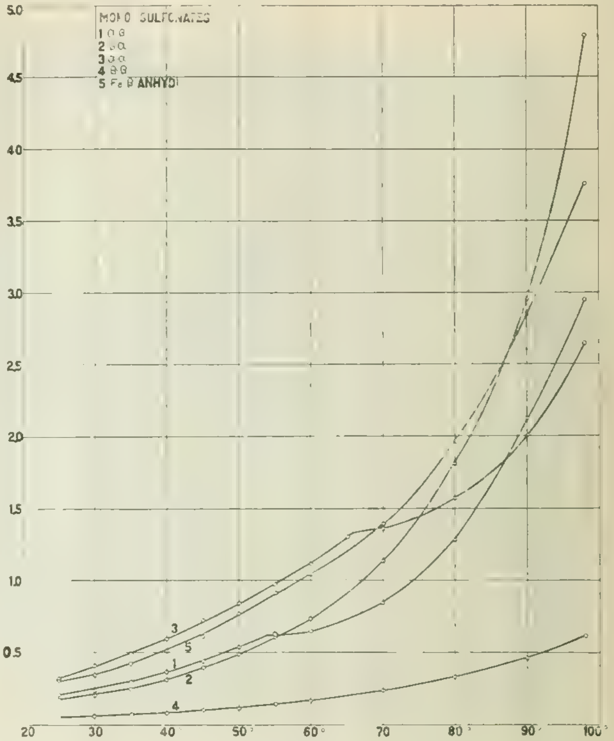
2,7
Pros-



1,6
Epi-

show clearly that the *ana-* and *amphi*-acids are the most symmetrical. The influence of the base apparently determines which shall be the least soluble. The *epi*-compound, on the other hand, shows no symmetry and is found to give the most soluble salts with both α- and β-naphthylamine. The *pros-* compound, while showing the symmetry of neither the *ana-* nor *amphi*-isomers, has symmetry about the line of the two common carbon atoms and, as would be expected, is more soluble than either of the latter but less soluble than the *epi*-compound.

The curve for α-naphthylamine naphthalene-β-sulfonate shows an allotropic change at about 54° C. and that for α-naphthylamine naphthalene-α-sulfonate, one at about 66° C. These allotropic forms have not yet been isolated. The forms described by Ambler are probably represented by the lower parts of these curves. When a solution of β-naphthylamine naphthalene-α-sulfonate is saturated at the boiling point and cooled rapidly without stirring, a stiff jelly is formed, which, if disturbed, will quickly change to the crystalline variety. The solubility measurements, however, gave no evidence of a transition point below 100° C. The curve for the ferrous salt of the naphthalene-β-sulfonate is also shown as this compound is the one used to identify the β-acid. Although this salt crystallizes at ordinary temperatures with six molecules of water of crystallization, and no break was found on the solubility curve, it was thought advisable to express all values in terms of the anhydrous salt.



Solubilities of Some Amino Salts of Naphthalenesulfonic Acids in Grams per 100 Grams of Solvent (0.01 *N* HCl)

α-Naphthylamine Salts

° C.	α-1,5	α-1,6	α-2,6	α-2,7
25	0.0605	2.29	0.5170	0.8689
30	0.0694	3.20	0.6082	0.9805
35	0.0853	4.21	0.7178	1.162
40	0.0972	7.15	0.8943	1.364
45	0.1033	9.59	1.005	1.599
50	0.1253	...	1.161	1.931
55	0.1563	...	1.288	2.405
60	0.1638	...	1.462	3.386
70	0.2212	...	2.062	10.3
80	0.2902	..	2.881	35.2
90	0.4010	...	3.770	87.7
98	0.4635	...	4.724	...

β-Naphthylamine Salts

° C.	β 1,5	β-1,6	β-2,6	β-2,7
25	0.0727	0.2952	0.0296	0.1327
30	0.0765	0.3898	0.0386	0.1454
35	0.0887	0.4934	0.0412	0.1917
40	0.1107	0.5600	0.0422	0.2160
45	0.1233	0.6789	0.0594	0.2737
50	0.1493	0.8105	0.0614	0.3312
55	0.1701	0.9546	0.0702	0.4241
60	0.1882	1.245	0.0806	0.4684
70	0.2562	1.852	0.1093	0.6791
80	0.3204	2 695	0.1626	0.9735
90	0.4427	4.019	0.2207	1.433
98	0.5887	5.726	0.2943	1.861

Monosulfonates

° C.	α-α	α-β	β-β	β-α	Fe-β (anhyd.)
25	0.3125	0.2039	0.0563	0.1735	0.3022
30	0.4131	0.2391	0.0599	0.2078	0.3470
35	0.5007	0.2985	0.0736	0.2533	0.4233
40	0.5991	0.3675	0.0816	0.3150	0.5135
45	0.7340	0.4420	0.1008	0.3985	0.6174
50	0.8356	0.5398	0.1171	0.4954	0.7711
55	0.9733	0 6246	0.1434	0.6044	0.9171
60	1.113	0.6542	0.1656	0.7391	1.056
65	1 305	......	......	.. ..	.....
70	1.368	0.8493	0.2393	1.141	1.393
80	1.571	1.283	0.3395	1.829	1.985
90	2.028	2.132	0.4667	2.980	2.882
98	2.651	2.951	0.6218	4.790	3.764

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[6] The only exception found was that of the dinitrobenzenes with water as a solvent.

Solubility of Sulfur in Rubber[1,2]

By C. S. Venable and C. D. Greene

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

The degree of solubility of free sulfur in rubber under various conditions has a practical as well as a theoretical interest. For example, this solubility is one of the two determining factors in the well-known phenomenon of "blooming." The presence of an excess of free sulfur unquestionably plays an important role in the aging of rubber goods. Furthermore, a number of theories as to the mechanism of vulcanization presuppose as the first step the melting of the sulfur and its solution in the rubber, and involve a difference in solubility of free sulfur as vulcanization proceeds.

The following paper records preliminary work on this important subject. The solubility of sulfur in rubber apparently increases slowly with the vulcanization coefficient, more rapidly as the temperature increases. With a coefficient greater than 7 per cent combined sulfur, solubility values could not be obtained by the method used because the rubber became almost impermeable to free sulfur. This impermeability probably has much more to do with the non-blooming of hard rubber stocks than has the slightly increased solubility for free sulfur.

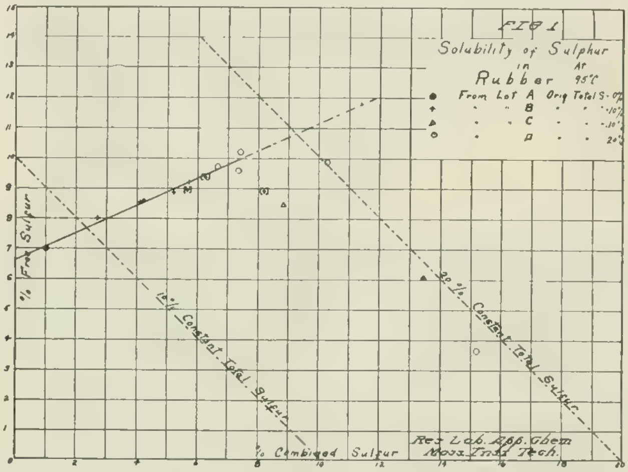
In spite of the importance of the subject, no quantitative data have been published on the solubility of sulfur in rubber. Practically the only results recorded are those of Skellon,[3] who placed together thin sheets of rubber containing different amounts of rubber and heated them to the vulcanization temperature. By analyzing for free sulfur he determined in which direction the sulfur had migrated. Obviously, he could thus obtain only approximate limits for sulfur solubility. The maximum solubility at 130° to 140° was apparently at about 10 per cent sulfur, and the solubility increased with the degree of vulcanization, a point of view which has often been taken in explaining the non-blooming of hard rubber. Skellon did show that the sulfur distributed itself fairly rapidly through the rubber in all directions. It is, of course, known that the solubility decreases as the temperature is lowered.

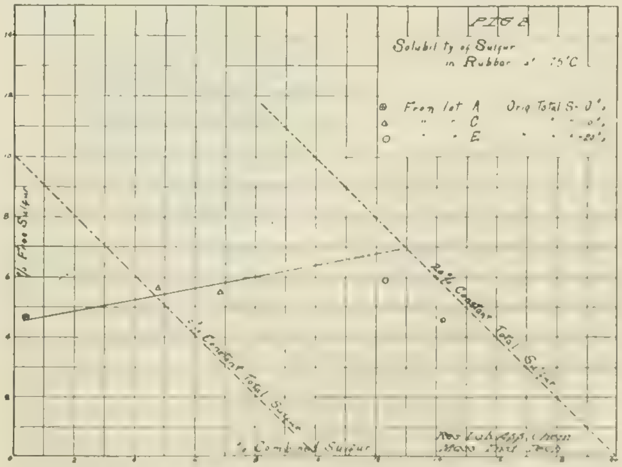
In order to secure more definite information, the following investigation was carried out in connection with some coöperative work for the Goodyear Tire and Rubber Company and is now published with their permission. The experimental determination of these solubility figures was a rather difficult problem. Even the best procedure which this Laboratory was able to develop did not give satisfactory results at any temperature for values of combined sulfur exceeding 7 per cent, and there is some doubt about several points obtained at the lower temperatures for values of combined sulfur less than 7 per cent. The results must therefore be considered as preliminary, but their publication seems desirable in view of the existing lack of information.

Procedure

The method adopted was to pack in flowers of sulfur thin strips of rubber stock that had been compounded with different amounts of sulfur (0 to 20 per cent on the weight of rubber used), and to keep the pack at the desired temperature until equilibrium was established between strip and sulfur. The samples were then analyzed for free and combined sulfur.

Equilibrium was approached from above and below, that is, from an excess and a deficiency of original free sulfur. If the sample contained a deficiency of free sulfur, sulfur migrated in and equilibrium was fairly quickly established. On the other hand, if the original sample possessed a large excess of free sulfur, usually present as crystals within the rubber, little if any of the excess sulfur migrated to the outside of the sheet. Consequently, all samples were given a preliminary heating at 120° C. to insure complete solution of the crystals before placing in the pack. It is common experience that, in the absence of crystallization centers within the rubber, a supersaturated solution forms, and the excess sulfur tends to migrate to the outside until equilibrium is approached. This short heating at 120° was repeated when the sample had apparently reached equilibrium to make sure that no crystallization centers had re-formed while the rubber was in the pack. In either case, the equilibrium point was determined either by a constancy in weight of sample after short intervals of heating, or better still by a practical constancy in values of free sulfur upon analysis of the samples from time to time.





It should be emphasized that the quantities of free sulfur found by the above procedure should represent the amount held in solution by the rubber in equilibrium with solid sulfur

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[1] Presented before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 44 from the Research Laboratory of Applied Chemistry, M. I. T.

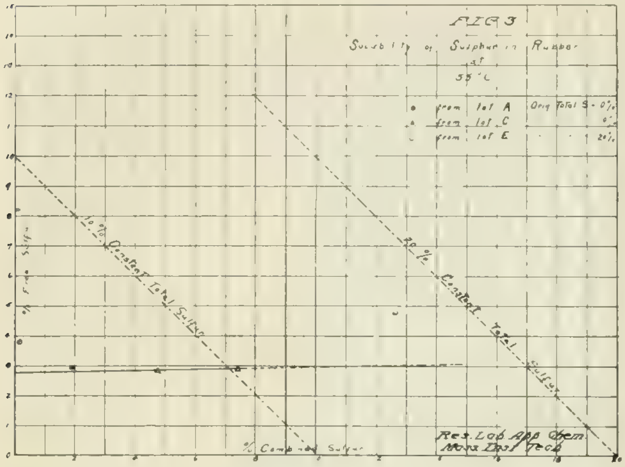
[3] *Kolloid Z.*, **14** (1914), 96.

at the same temperature; in other words, the true solubility of sulfur in rubber.

ANALYTICAL METHODS

The following analytical procedures were adopted:

FREE SULFUR—The method used was essentially that developed by W. J. Kelly[4] of the Goodyear Company.



The acetone solution obtained by a 16-hr. extraction of the sample was evaporated to a sirupy consistency and extracted with 75 per cent alcohol (saturated with sulfur) to remove resins and acetone-soluble sulfides. The residual sulfur was freed from alcohol, oxidized with bromine-carbon tetrachloride and zinc oxide-nitric acid solutions, and weighed as barium sulfate.

COMBINED SULFUR—The residue from acetone extraction was refluxed for 8 hrs. with alcoholic sodium hydroxide to remove any acetone-insoluble sulfur compounds other than polyprene sulfide. If zinc oxide had been present in the original samples, the residue was repeatedly evaporated with dilute hydrochloric acid until evolution of hydrogen sulfide had ceased. The final residue was oxidized with zinc oxide-nitric acid and bromine-nitric acid, and the sulfur was weighed as barium sulfate.

All results are reported in grams of sulfur per 100 g. rubber.

SAMPLES USED

The rubber used was smoked sheet, in strips about 1 mm. thick and compounded by weight as follows:

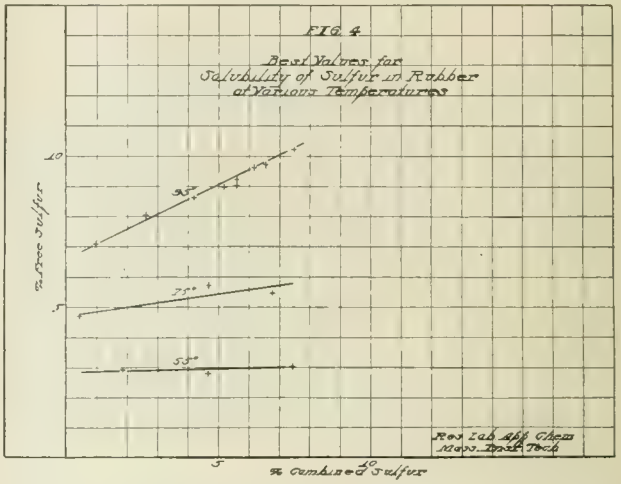
LOT NO.	DESCRIPTION
A	Smoked sheet, unvulcanized
B	Smoked sheet, 100; sulfur, 10; thiocarbanilide, 3
C	Smoked sheet, 100; sulfur, 10; zinc oxide, 10; thiocarbanilide, 3
D	Smoked sheet, 100; sulfur, 20; thiocarbanilide, 3
E	Smoked sheet, 100; sulfur, 20; zinc oxide, 10; thiocarbanilide, 5

Samples B, C, D, and E were vulcanized to coefficients varying from 1 to 8 per cent combined sulfur before placing in the sulfur pack. For a given solubility determination, a sample was chosen with a vulcanization coefficient close to that desired.

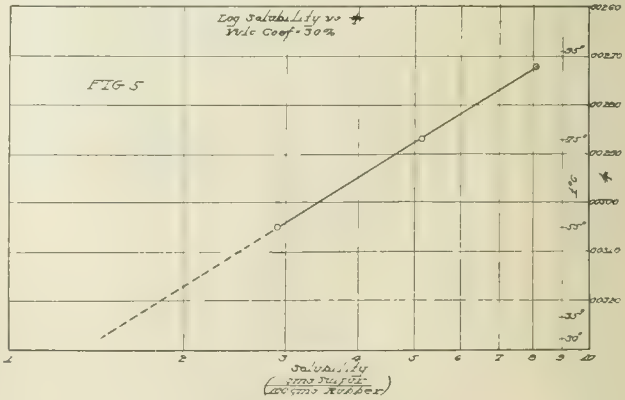
EXPERIMENTAL RESULTS

In Figs. 1 to 3 are plotted values found for free sulfur (sulfur in solution) against vulcanization coefficient at 95°, 75°, and 55°, respectively. Inasmuch as these values were approached from an original total sulfur content of 0, 10, or 20 per cent, lines have been drawn on each diagram for 10 per cent and 20 per cent total sulfur contents. In other words, these lines show how the free sulfur would have varied with the degree of vulcanization had there been no diffusion of sulfur into or out of the sample.

SOLUBILITY AT 95° C.—At 95° the solubility curve appears to be a straight line function of the amount of combined sulfur, up to a vulcanization coefficient of about 7 per cent. At this point the curve breaks. No reliable data could be obtained for the harder stocks. Apparently, the migration of sulfur in either direction is markedly retarded by the increasing hardness of the stock. This is indicated by the fact that total sulfur becomes nearly constant. For example, the bracketed points represent successive determinations made on a sample from Lot B after different intervals of heating. The points corresponding to a combined sulfur content of 5.7 and 6.3 per cent follow closely the solubility line. However, the point corresponding to a combined sulfur content of 8.2 per cent drops along a line of constant total sulfur content. In general, for a stock with a combined sulfur content exceeding 7 per cent, it was found impossible to check free sulfur values by using stocks containing different amounts of total sulfur, as was done with stocks vulcanized to a combined sulfur content of less than 7 per cent.



SOLUBILITY AT 75° C.—The solubility curve at 75° C. was determined from a smaller number of points, but the same relationship apparently holds. The solubility is apparently a straight line function up to a combined sulfur content of about 7 per cent. Beyond this point, migration of sulfur is apparently retarded, and no reliable data were obtained.



SOLUBILITY AT 55° C.—It was thought that the time required to reach equilibrium at this temperature might be decreased by heating the samples in sulfur at 95° C. for 4 hrs. before putting them in the 55° bath. The sample from Lot A gained a large excess of sulfur which could not be completely removed even by subjecting the sample to alternate heatings at 120° and 55° C. The last point obtained was apparently in error, owing to the same difficulties in sulfur migration as were noted at the higher temperatures. There was little reason to doubt the accuracy of the three other points, and the line was drawn as indicated.

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[4] THIS JOURNAL, **14** (1922), 196.

HEAT OF SOLUTION—Solubility values for the rubber stocks having a vulcanization coefficient up to 7 per cent have been plotted in Fig. 4 for the three temperatures. That the curves are reasonably consistent is indicated by the fact that if, for any vulcanization coefficient, the log of the solubility is plotted against the reciprocal of the absolute temperature, the result is a straight line. From such a diagram drawn for a combined sulfur content of 3 per cent (Fig. 5), neglecting heat of dilution (which is probably small), it can be calculated that the molal heat of solution of sulfur in rubber between 55° and 95° C. is 6200 cal. Assuming the molecular condition of sulfur in rubber to be S_8, as it is in most organic solvents, the heat of solution of 1 g. of sulfur in 100 g. of rubber becomes 24.2 cal.

It should be noted that at room temperature there is apparently not a very great difference in the solubility of sulfur in soft and hard rubbers. The indications are, therefore, that the non-blooming of hard rubber stocks at room temperature should be attributed more to the retarded migration of the sulfur than to any increased solubility for the sulfur.

SOLUBILITY AT 140° C.—The solubility of sulfur in rubber at vulcanization temperature, or 140° C., is of considerable practical interest. This value cannot be obtained directly by extrapolation of the line in Fig. 4 to 140° C., on account of changes in slope at 96.5° C., where rhombic sulfur changes to monoclinic, and at 119° C., where monoclinic sulfur melts to liquid sulfur. Theoretically, these changes in slope can be calculated from the heat quantities involved, but it is necessary to make several assumptions (for example, that the molecular condition for dissolved sulfur over this range is unchanged), which make a solubility figure thus obtained of doubtful value. From an inspection of such a diagram and of the vapor pressure curves of the various forms of sulfur over the same range, it would seem that the solubility of sulfur in rubber at 140° C. is about 20 g. of sulfur per 100 g. rubber. This figure should be checked experimentally.

The Hygroscopicity of Picric Acid[1,2]

By L. Grier Marsh[3]

Explosives Chemical Laboratory, Bureau of Mines Experiment Station, Pittsburgh, Pa.

Pure picric acid is only slightly hygroscopic. The purified product, crystallized from water, absorbs from 0.25 to 0.37 per cent moisture in a saturated atmosphere at 32° C. during 48 hrs. The hygroscopicity of the commercial material is dependent upon its purity, or the presence of water-soluble materials. Picric acid containing as much as 0.05 per cent SO_3 (present as sulfate or free sulfuric acid) exposed in a saturated atmosphere at 32° C. for 48 hrs., increased 1.9 per cent in weight; under the same conditions, containing 0.16 per cent of SO_3, the increase was about 5 per cent.

At the close of the war the United States Government had on hand, and still has, large quantities of picric acid, of which it is endeavoring to dispose for industrial purposes. The value of picric acid as an explosive has been discussed by Munroe and Howell,[4] and as its industrial utility might be affected by its tendency to absorb moisture, the former suggested that the hygroscopic properties of the explosive be determined. The hygroscopicity of TNT had already been investigated by Huff[5] in the explosives chemical laboratory of the Bureau of Mines, and the writer followed his method for picric acid.

Theoretical

The behavior of any salt, not forming crystalline hydrates, toward atmospheric moisture is dependent upon the solubility of the salt in water, and follows simple physicochemical laws. If the partial pressure of the water vapor in the air exceeds the vapor pressure of the saturated solution of the salt, the salt will absorb moisture from the air; but if the partial pressure of the water vapor in the air is less than the vapor pressure of the saturated solution of the salt, no moisture will be absorbed by the salt; on the contrary, it will lose water to the air. By knowing the solubility of such a salt in water, the vapor pressure of its saturated solution at this particular temperature can be calculated by Raoult's Law, and from this the hygroscopicity of the salt may be determined.

From the nature of organic crystalline compounds, it is evident that their hygroscopicity is generally comparatively low. The rate of moisture absorption by TNT was found by Huff to be practically nil (less than 0.01 per cent). While no data on the hygroscopic properties or vapor pressures of saturated solutions of picric acid are available, the solubility of the compound in water at different temperatures has been fairly extensively investigated, and from this the measurement of its vapor pressure and hygroscopicity can be calculated.

Calculated Hygroscopicity

According to Findlay[6] the solubility of picric acid in water is in part as follows:

Temperature ° C.	Solubility Per cent
0	1.05
5	1.07
10	1.10
15	1.16
20	1.22
25	1.37
26.5	1.42
30	1.55
40	1.98

At 32° C. the solubility of picric acid in water is assumed to be 1.636 per cent, and at the same temperature the vapor tension of water is given by Broch and Weibe[7] as 35.372 mm. of mercury. From Raoult's Law, embodied in the formula

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N + n}$$

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[1] Received January 16, 1922.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Assistant Explosives Chemist, Pittsburgh Experiment Station, Bureau of Mines.

[4] "Picric Acid as an Explosive," *Bur. Mines, Serial* **2243**, April 1921.

[5] "The Hygroscopicity of TNT," *Chem. Met. Eng.*, **21** (1919), 570.

[6] *J. Chem. Soc.*, **81** (1902), 1219.

[7] Olsen, Van Nostrand's Chemical Annual, **1918**, 532.

where p_1 and p_2 denote the vapor pressures of solvent and solution and n and N the number of moles of solute and solvent, respectively, the vapor pressure of a saturated solution of picric acid at 32° is found to be 35.3265 mm. of mercury, or 99.872 per cent of that of pure water. Since these are very nearly equal, it follows that picric acid is only slightly hygroscopic. (Incidentally, this hygroscopicity must be multiplied 62.5 times to become equal to that of potassium nitrate and 187.5 times before it would be necessary to enclose it in waterproofed inner packages.)[8] According to Huff,[6] at 25° TNT is $\frac{1}{2300}$ as hygroscopic as potassium nitrate.

EXPERIMENTAL

Commercial picric acid nearly always contains impurities and occasional adulterations, but in practically negligible quantities. Sodium sulfate is sometimes added before crystallization, while occasionally[9] oxalic acid and sugar have been reported. Free sulfuric acid is also a common impurity, and it is possible that a nitrophenolsulfonic acid exists in the lower grades of the explosive.

Since small quantities of water-soluble impurities will necessarily affect the hygroscopic properties of any crystalline compound which is only slightly soluble in water, laboratory experiments were made on two different grades of commercial picric acid, as well as on the pure material. The latter was prepared by crystallizing from solution in hot water three times, washing the crystallized product thoroughly with cold water each time. For comparative purposes, the rate of moisture absorption of potassium perchlorate was also determined at the same temperature. The method used by Taylor and Cope[10] was followed.

The picric acid was exposed in open porcelain crucibles (2 cm. deep with flat bottoms 3.7 cm. in diameter, so that the 2-g. sample taken covered about 11 sq. cm. of surface) over water under carefully regulated conditions, and the increase in weight noted after various intervals. Ordinary quart jars, hermetically sealed with glass tops and spring clamps, were filled 2 cm. deep with distilled water, and in each jar was placed a small copper tripod to hold one crucible. The jars were then submerged under water in a large thermostat, and allowed to remain until the contents came up to the bath temperature. When sufficient time had elapsed for this, the jars were slightly elevated until the necks emerged, the glass tops removed, and the crucibles with contents placed on the small tripods within. The jars were then tightly closed as before, submerged, and allowed to remain for the periods desired. In order to prevent possible condensation of moisture, the crucibles were warmed slightly above the bath temperature before being placed in the jar.

TABLE I

	Pure	Commercial No. M-2308	Commercial No. M-2330
Melting point, ° C.	121.5–122.5	119.5–121.0	120.0–121.0
Solidification point, ° C.	121.5	120.7	120.0
Moisture, per cent	0.00	0.00	0.00
Insoluble matter, per cent	0.00	0.002	0.002
Sulfur trioxide, per cent*	0.00	0.16	0.049
Nitrates, per cent	0.00	0.00	0.00
Ash, per cent	0.00	0.001	0.002

* The sulfur trioxide was present as a sulfate or free sulfuric acid.

The thermostat was a large tank of water, 30 × 26 × 20 in., heated by electric coils, electrically stirred, and controlled by a toluene thermoregulator within a range of 0.1°. The jars were kept practically at constant temperature (32° C.) throughout, and constant conditions of humidity, with the prevention of moisture condensation on the walls, were assured. Blank tests on empty crucibles were run at the same time. When a crucible was taken from a jar it was covered immediately with a porcelain lid, whose weight was known, and weighed as rapidly as possible.

Analyses of the different samples of picric acid are given in Table I.

These samples were carefully dried in a desiccator over sulfuric acid for 3 days before the analyses and hygroscopicity tests were made. Results on the rate of moisture absorption are given in Table II.

TABLE II—APPARENT RATE OF MOISTURE ABSORPTION IN SATURATED ATMOSPHERE AT 32° C.

MATERIAL	HOURS	Increase Grams	Increase after Deducting for Crucible Per cent
Pure picric acid	5	0.0051	0.15
	17	0.0068	0.20
	24	0.0076	0.25
	41	0.0084	0.31
	48	0.0099	0.37
Commercial picric acid, M-2308	5	0.0291	1.35
	17	0.0651	3.13
	24	0.0759	3.69
	41	0.0954	4.66
	48	0.1029	5.02
Commercial picric acid, M-2330	5	0.0113	0.46
	17	0.0209	0.96
	24	0.0256	1.18
	41	0.0354	1.61
	48	0.0407	1.91
$KClO_4$	5	0.0067	0.23
	17	0.0151	0.62
	24	0.0209	0.94
	41	0.0339	1.58
	48	0.0411	1.93
Empty crucible	5	0.0021	..
	17	0.0026	..
	24	0.0020	..
	41	0.0022	..
	48	0.0025	..

The above results are the average of five determinations.

DISCUSSION OF RESULTS

In comparing the solubility of potassium perchlorate and picric acid in water it is evident that the hygroscopicity of the former is greater, and increases more readily with rise in temperature than does that of picric acid. From Marshall's[11] table of "relative humidity" and "relative deliquescence" of different compounds the comparative hygroscopicity of different substances can be calculated. Potassium nitrate is taken as a standard, and the relative deliquescence of this substance is taken as 1. At a temperature of 32° C., the relative humidity of picric acid was previously found to be 99.872 per cent. This gives a relative deliquescence of 0.016. From a calculated solubility of 3.60 per cent[12] at 32°, of potassium perchorate in water, the relative humidity and relative deliquescence can be similarly determined as 99.532 and 0.0585. Theoretically then, potassium perchlorate should deliquesce about 3.7 times more rapidly than does picric acid at a temperature of 32° C. On examination of the results obtained, the deductions seem to be well verified, showing that the method gives results coming well within the range of experimental accuracy.

ACKNOWLEDGMENT

The writer wishes to acknowledge the constructive suggestions and helpful criticisms given by Dr. C. E. Munroe of the National Research Council, A. C. Fieldner, Supervising Chemist, and C. A. Taylor, Explosives Chemist of the Bureau of Mines, in the preparation of this article.

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[8] Arthur Marshall, "Explosives, Their Manufacture, Properties, Tests, and History," **1915**, 340.

[9] Marshall, *Loc. cit.*, 576.

[10] "Hygroscopic Properties of Sodium, Potassium, Ammonium Nitrate, Potassium Chlorate and Mercury Fulminate," *Chem. Met. Eng.*, **15** (1916), 140.

[11] *Loc. cit.*, 340.

[12] Comey-Hahn, "Dictionary of Chemical Solubilities—Inorganic."

Failure of Cast and High Silicon Iron in Fuming Sulfuric Acid[1]

By T. F. Banigan

Hercules Powder Company, Hercules, California

Experiments carried out by the writer on metallic silicon and silicon-iron alloys indicate that the failure of cast iron and malleable castings in fuming sulfuric acid is due to oxidation of the particles of silicon in the casting to particles or crystals of silicon dioxide, which, being larger in volume than the original silicon particles, place the casting in a condition of internal strain.

Cast iron, with as low silicon content as ordinary steel, should be as satisfactory as the latter for use with fuming sulfuric acid, and any reduction in silicon content should improve it for this use.

It is frequently desirable in the manufacture and use of fuming sulfuric acid to employ cast-iron equipment, but castings of this material are likely to crack suddenly after being used for considerable periods of time with either hot or cold sulfuric acid containing free SO_3. Cracking also occurs, to a less degree, with anhydrous mixtures of nitric and sulfuric acids and is considerably more severe with hot than with cold acids.

Numerous cases have come to the attention of the writer where heavy cast-iron pipes used with fuming sulfuric acid, in places where they were exposed to no unusual strains, have cracked longitudinally with loud reports, though the pipes on later examination showed practically no evidence of corrosion by the acid. Similarly, cast-iron valves and pumps in such service crack from no apparent cause before the metal shows sufficient wear to account for such failure. Malleable castings used in attempts to overcome this difficulty have failed likewise. Breaks in such pieces of equipment while in operation involve such serious danger to human life, loss of material, and stoppage of production that some manufacturers eliminate the danger by substituting steel, which is more expensive but free from this defect.

Lunge[2] quotes Knietsch, in explanation of this peculiarity of cast iron as follows:

> Whereas cast-iron vessels are very suitable for the manufacture of hydrated sulfuric acid, this is not the case for fuming acids, for these, although they corrode the metal but slightly, cause it to crack, sometimes quite suddenly with a loud report. Evidently the fuming acid penetrates into the pores of the metal, where it is reduced to SO_2 and H_2S, with formation of CO_2 from the carbon of the cast iron—all of them gases with somewhat low critical temperatures which produce high tensions in the interior of the metal.

EXPERIMENTAL

EXPT. 1—Test bars of a well-known high-silicon iron alloy, which is extremely resistant to nonfuming sulfuric acid, were immersed in 15 per cent oleum, or 103.37 per cent H_2SO_4 at room temperature for 19 days. The bars were then washed with water and found to be severely corroded and covered with gelatinous silica. Loss in weight amounted to 4.73 per cent. The sludge produced in this test was found to contain a considerable amount of free carbon.

EXPT. 2—A weighed quantity of amorphous silicon was introduced into 103.37 per cent H_2SO_4 and kept at about 92° C. for 8 days. The mixture was then drowned in distilled water and filtered through a weighed Gooch crucible which was then heated at less than dull red heat and weighed. The increase in weight was calculated to SiO_2. Filtration was difficult on account of the gelatinous silica present. Increase in weight showed that 24.64 per cent of the total silicon had been oxidized to SiO_2.

EXPT. 3—A weighed quantity of amorphous silicon was treated as in Expt. 2 except that it was allowed to stand at room temperature for 21 days. Increase in weight corresponded to 40.20 per cent of total silicon oxidized to SiO_2.

EXPT. 4—In order to determine with certainty that the increase in weight of silicon in the preceding experiments was due to action of the free SO_3, a weighed amount of amorphous silicon was kept for 8 days at 100° C. in 96 per cent H_2SO_4. No increase in weight resulted.

EXPT. 5—A sample of silicon carbide was introduced into 103.37 per cent H_2SO_4 and heated at 100° C. for 7 days. No change in weight resulted.

CONCLUSIONS FROM EXPERIMENTS

1—Silicon either in free condition or alloyed with iron is readily oxidized by sulfur trioxide.

2—The failure of high-silicon iron alloys in fuming sulfuric acid is due to rapid oxidation of silicon to the more voluminous SiO_2 which tears down the surface of the casting, thereby continually exposing fresh surface to the action of the SO_3.

3—The failure of cast iron and malleable iron in fuming sulfuric acid is apparently due to SO_3 penetrating into the pores of the casting and oxidizing the silicon to SiO_2, which, on account of its large volume, produces a condition of internal strain. Action of SO_3 on silicon carbide in the casting is not responsible for failure. Carbon in the casting appears to be little, if at all, affected under these conditions, and in the usual amounts probably has no injurious effect.

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[1] Received November 17, 1921.

[2] "Sulfuric Acid and Alkali," 4th edition, Vol. 1, Part 1, 322.

Retirement of E. G. Rippel

E. G. RIPPEL

Mr. E. G. Rippel, who organized the Buffalo Foundry and Machine Company about twenty-one years ago, has recently retired from active duty as sales manager of the corporation. Mr. Rippel has always believed in a progressive development policy, to which our chemical industry is indebted for many important pieces of plant apparatus. He has been an ardent supporter of the National Exposition of Chemical Industries and is to be credited with considerable contributions toward its success.

After a much-needed rest, plans for the future may be announced by Mr. Rippel.

Determination of Esters in Imitation Flavoring Extracts[1,2]

By George F. Beyer

Industrial Alcohol and Chemical Division, Bureau of Internal Revenue, Treasury Department, Washington, D. C.

The following paper describes the method developed and used by the Bureau of Internal Revenue for the determination of esters in imitation flavoring extracts. All commonly used esters are completely recovered by distillation with 50 per cent alcohol, provided the receiving flask is properly closed with a mercury trap valve. All imitation flavoring extracts should be distilled before total esters are determined, since reducing sugars which may be present will react with the alkali. Water is not a satisfactory saponification medium.

The fixing of certain standards to which imitation flavoring extracts manufactured under the provisions of the National Prohibition Act must conform has raised some questions as to the analytical methods best employed in determining the ester content of such extracts. It has therefore seemed desirable to review the methods for ester determination commonly employed, with a view to determining the best analytical method to be used. It is furthermore desirable that the manufacturing interests concerned be acquainted with the method now used in the laboratories of the Bureau of Internal Revenue in order that they may properly supervise their manufacturing operations.

Preliminary Investigation

Solutions were made up containing only one ester or containing mixtures of esters commonly used. With only one ester a 2 to 4 per cent solution in 50 per cent of ethyl alcohol was employed. Solutions containing from 4 to 10 per cent of mixed esters in 50 per cent of alcohol were used for the composite mixtures. The principal esters used were ethyl acetate, amyl acetate, amyl butyrate, amyl valerinate, oenanthic ether, and sebacic ether. The composite mixtures were:

A	Cc.
Amyl butyrate	2
Ethyl acetate	2
Ethyl butyrate	1
Sebacic ether	1
Amyl acetate	4

B	
Amyl butyrate	2
Amyl valerinate	2
Amyl acetate	2
Pelargonic ether	1
Oenanthic ether	1

C	
Amyl valerinate	5
Amyl acetate	4
Amyl butyrate	5
Oenanthic ether	1
Pelargonic ether	1
Sebacic ether	2
Ethyl butyrate	3
Ethyl acetate	2
Ethyl benzoate	1

These three mixtures were made up to 250 cc. at 60° F. in sufficient alcohol and water to effect solution.

SAPONIFICATION MEDIA—The first point to be considered was the best medium for completeness of saponification. This was tested by the A. O. A. C. method, without distillation. When water was used as the saponification medium with 10-cc. portions of the single and composite ester mixtures, the results were low. The addition of 25 cc. of 95 per cent ethyl alcohol as a saponification medium gave results practically in accordance with the calculated content of esters present.

TIME REQUIRED—Solutions of ethyl acetate showed 96 per cent saponification after 5 mins.' refluxing on the steam bath and complete saponification after 10 mins.' refluxing. The same solution was allowed to stand with alkali in a tightly stoppered flask, at room temperature, and shaken well every 5 min. for 0.5 hr. Another solution was allowed to stand at room temperature in a tightly stoppered flask in the presence of alkali over night. Saponification was complete in both cases.

A similar series of experiments with amyl acetate disclosed the fact that 94 per cent of the ester was saponified by refluxing for 5 min. over the steam bath, and saponification was complete in 10 min. The similarity of the results obtained with amyl acetate seem to offer additional proof of the theory of ester transposition, that is, that amyl acetate in the presence of a large excess of ethyl alcohol and alkali is transposed into ethyl acetate and amyl alcohol before saponification begins, it being a well-known fact that the speed of the reaction of the transposition is many times more rapid than the saponification of the ester.

Ten-cc. portions of ethyl acetate, amyl acetate, and amyl butyrate mixtures were allowed to stand over night with an excess of standard alkali, and were finally refluxed for 0.5 hr. on the steam bath. Other 10-cc. portions of the same mixtures were immediately refluxed on the steam bath for 0.5 and 1 hr., respectively. Saponification was complete in each instance.

Ten cc. of an imitation peach extract of known composition were treated in a similar manner. It was found that in all cases more complete saponification was obtained when the solution was allowed to stand over night before refluxing for 0.5 hr. on the steam bath. The low results obtained from immediate refluxing were attributed to the probable escape of some of the esters through the air condenser. It was also possible that the saponification of the imitation peach extract was incomplete, but the fact was not definitely determined.

Pardee and Reid[3] have shown that it is impossible to obtain results which are concordant or even close to 100 per cent of the ester present when certain esters are saponified in methanol by refluxing for 1 hr. on the steam bath with the ordinary 3-ft. air condenser. They attribute this to the escape of the ester through the condenser.

One experiment was undertaken to see if this possible loss through the air condenser could be prevented. Two 5-cc. portions of a 4 per cent solution of amyl acetate in methyl alcohol were saponified in methanol as the saponification medium. One portion was refluxed immediately for 0.5 hr. on the steam bath; the other was allowed to stand in a tightly stoppered flask at room temperature for 1 hr., with thorough shaking every 5 min., and then refluxed for 0.5 hr. on the steam bath. Approximately 98 per cent of the calculated amount was found when the solution was refluxed immediately, while practically 100 per cent were found in the other case.

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[1] Received November 10, 1921.

[2] Published by permission of the Commissioner of Internal Revenue.

[3] This Journal, 12 (1920), 129.

RECOVERY OF ESTERS—To determine whether the esters could be recovered by distillation, the mixtures were again used. Ten-cc. portions of the solutions were diluted with 100 cc. of water and distilled until 100 cc. of distillate were collected. Saponification of the distillates gave low results in all cases. Ten-cc. portions were then diluted with 100 cc. of 50 per cent ethyl alcohol and distilled until 100 cc. were collected. Saponification of the distillates showed that, although all the results were a little low, they were substantially higher than when water was used for dilution. The ethyl acetate solution showed a lower recovery than any other. In all cases the residues in the distillation flasks were saponified and no esters were found.

Since there was a fairly high recovery of the ester by distillation with 50 per cent alcohol and none was left in the distilling flask, it seemed possible that the loss might be due to escape of a portion of the more volatile esters in the condenser. The fact that the loss was greatest with ethyl acetate seemed to support this view. In order to settle this point a mercury valve was placed in the Kohlrausch flask, which was used as a receiving flask, and the flask itself placed in ice water and protected from the heat of the burner. Even in the case of ethyl acetate recovery was now practically complete. With amyl acetate and amyl butyrate and the various mixtures used recovery was complete. A number of distillations with 35 per cent alcohol as the diluting mixture gave lower results than when the 50 per cent solution was used.

Ten cc. of Mixture A, to which 100 cc. of 50 per cent alcohol were added, were distilled from an ordinary round-bottomed, side-necked distilling flask carrying a thermometer to ascertain the distillation temperature. Below 103° C., 108 cc. distilled over. The first 75-cc. portion of the distillate and the last 33-cc. portion were saponified separately. The first 75 cc. of the distillate contained practically all of the esters. Later experiments showed that the first 80 cc. of the distillate contained all of the esters.

SIZE OF SAMPLE—The present standard of the Internal Revenue Bureau requires in certain imitation extracts not less than 5 g. of esters per 100 cc., calculated as ethyl acetate. This obviously requires the addition of more than 5 g. of esters per 100 cc. where esters of higher molecular weight than ethyl acetate are used.

Determinations were made on 5 cc. of the Mixture C, containing higher molecular weight esters. There was practically no difference in the results obtained whether 5 or 10 cc. of the same were taken.

A number of imitation extracts found on the market were saponified before and after distillation with 50 per cent alcohol. In a number of samples it was found that considerably higher results were obtained when they were saponified without distillation. Others showed no difference. It was concluded that in the former case some substance was present with the ester that reacted with the alkali. Upon evaporation to dryness over the steam bath it was found that these samples contained a reducing sugar. When a 5 per cent solution of glucose was digested with an excess of standard alkali solution on the steam bath for 1 hr., a substantial amount of alkali was consumed. It was apparent, therefore, that distillation after dilution with 50 per cent alcohol solution was necessary in order to obtain correct results.

DENATURED ALCOHOL—Specially denatured alcohol, Formula 30 (100 parts of pure ethyl alcohol and 10 parts of refined methanol), was used in place of pure ethyl alcohol. The results were the same as when pure ethyl alcohol was used. This point is noted merely for the information of laboratories who use this formula of tax-free alcohol.

It was further found that many of the so-called pure esters upon the market contain only 90 per cent of the ester itself.

The following method is now being used by the Bureau of Internal Revenue.

METHOD

Introduce 100 cc. of 50 per cent (by volume) ethyl alcohol (or specially denatured, Formula 30) into a 500-cc. Erlenmeyer flask and add 10 cc. of the extract (5 cc., in extracts containing as much as 5 per cent calculated as ethyl acetate). Connect the flask by means of a "gooseneck" with a vertical condenser, the end of which is fitted with a rubber stopper carrying a mercury valve. Attach a 100-cc. Kohlrausch flask to this rubber stopper, and distil the solution slowly until 100 cc. of distillate are collected. (It is very essential that the distillation apparatus be set up according to the above directions, as this reduces the loss from evaporation to a minimum.)

Transfer the distillate to a 500-cc. Erlenmeyer flask, rinsing the Kohlrausch flask with a few cc. of 50 per cent alcohol. Add about 5 drops of phenolphthalein solution and neutralize to a first pink color, then add 0.1 N NaOH in about 25 per cent excess of the amount necessary for complete saponification. Stopper the flask tightly and allow to stand over night at room temperature. Reflux for 0.5 hr. on a steam bath with an ordinary air condenser not less than 3 ft. in length. A piece of glass tubing, not too small, of the required length inserted in a rubber stopper makes an excellent condenser for this purpose. When the saponification is completed, cool rapidly to prevent the absorption of carbon dioxide from the air, and titrate the excess of sodium hydroxide with 0.1 N acid. A blank determination should be carried out simultaneously, using the same quantities of alcohol and alkali. After correcting for the blank, calculate results as ethyl acetate. Each cc. of 0.1 N alkali is equivalent to 0.0088 g. of ethyl acetate.

ACKNOWLEDGMENT

The author wishes to thank Arthur L. Morawski for assistance rendered in the work reported in this paper.

Our English Friends

The season at which Americans are accustomed to undertake European travel will soon be upon us and it seems proper to call attention to the unusually cordial relations which exist between the Chemical Industry Club, Whitehall Place, London, and the Chemists' Club of New York City. Both institutions desire to cultivate and provide for the social side of chemical industry and science by opening their doors to visiting members of either Club. This has not only promoted acquaintance and friendship on the part of chemists of both nations but is the means of favorable entrée in the two countries for those interested in industrial plants and laboratories. The letters which have been exchanged between Mr. H. Edwin Coley, for the Chemical Industry Club, and Dr. T. R. Duggan, Trustee of the Chemists' Club, convey warm and cordial greetings and assure a continuation of the kind feelings which have existed between the two Clubs and which should continue for many years.

A Memorial to Dr. Baskerville

The students of the day and evening sessions of the College of the City of New York, together with the staff of the chemistry department, have started a fund to establish a prize or scholarship in memory of Dr. Baskerville, head of the department of chemistry since 1904.

It is hoped ultimately to establish a Baskerville Research Scholarship in Chemistry, to be awarded annually to a student of the College. For the present it is planned to present an annual prize. Dr. Prager, College of the City of New York, St. Nicholas Terrace and 139th St., is in charge of the fund.

A. Ph. A. Research Grant

The American Pharmaceutical Association has available a sum amounting to $360.00 which will be expended after October 1, 1922, for the encouragement of research.

Investigators desiring financial aid in their work should communicate before June 1, with Prof. H. V. Arny, Chairman, A. Ph. A. Research Committee, 115 West 68th St., New York City, giving their past record and outlining the particular line of work for which the grant is desired.

First Report of the Committee on Contact Catalysis[1]

By Wilder D. Bancroft

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In certain cases of contact catalysis it is known that definite intermediate compounds are formed and Armstrong and Hilditch postulate the formation of ternary compounds. In other cases, it seems equally certain that no definite intermediate compounds are formed and that we are dealing with adsorption, which may mean formation of indefinite intermediate compounds. While it is very important to distinguish between these two types of contact catalysis and while this has not been done satisfactorily in the past, a determination of these points will not tell us why the reaction is accelerated, though it will give us important information about the mechanism of the reaction. For catalysis to occur the reacting substances must be converted rapidly into active modifications or into active compounds. It has been suggested by W. C. McC. Lewis, Perrin, and others that the catalytic agents emit infra-red radiations and that these radiations cause the catalysis. These ingenious speculations seem quite inadequate, however, to account for the phenomena.

It seems certain that in some way the catalytic agent activates one or more of the reacting substances, causing the opening and shutting of certain bonds or contravalences; but as yet we are not prepared to say which bonds or which contravalences are opened in any given case. This hypothesis makes possible a new, tentative explanation of the action of promoters. If the catalytic agent activates only one of the reacting substances or activates one chiefly, it is possible that the promoter activates or increases the activity of the other. If the given catalytic agent adsorbs or activates two substances in the wrong parts of the molecules, it may easily retard instead of accelerating the reaction; this case has been studied by Kruyt and van Duin.

While we are still very much at sea as to the way in which any given catalytic agent works, the theory of the poisoning of contact catalytic agents seems to be in very good shape. Any substance which retards, or prevents, the approach of the reacting substances to the catalytic agent will slow down or put an end to the reaction. Any strongly adsorbed solid, liquid or gas may therefore act as a catalytic poison. This should be distinguished from the cases in which the catalytic agent sinters together so as to have less surface or a more inactive surface. There is reason to suppose that a porous surface is essential and that a glazed surface is ordinarily quite inactive. While the poisoning of a catalytic agent is usually a thing to be avoided, Rosenmund and Zetsche have made successful use of what they call partial poisoning to stop a reaction at a given point.

It is evident that different catalytic agents activate certain molecules in different ways because alcohol decomposes almost completely to ethylene and water in presence of alumina or kaolin and almost completely to acetaldehyde and hydrogen in presence of pulverulent nickel. If we can determine what bonds or contravalences are opened by each catalytic agent we can probably predict the resulting reaction; but it is quite possible that we may have to reverse things and to deduce from the reaction products what bonds or contravalences were broken.

Rideal has attempted to connect overvoltage with contact catalysis, the overvoltage being primarily a measure of the energy necessary to desorb hydrogen gas from a metal surface; the metals show no catalytic activity when the energy necessary for desorption exceeds that necessary for the activation of hydrogen in the gaseous state in the absence of a catalytic material. This does not seem a very satisfactory point of view; a more plausible line of attack would seem to be that platinum catalyzes the reaction between atomic and molecular hydrogen, but establishes an equilibrium with some monatomic hydrogen remaining. This accounts for the low overvoltage and the distinct activation. Lead, mercury, and zinc do not catalyze the reaction; but the equilibrium lies entirely at the stage of molecular hydrogen. This accounts for the high overvoltage and the low catalytic action. The other metals come in between these two extremes and, at higher temperatures, the activating power of nickel and copper for hydrogen becomes greater than that of platinum. This set of hypotheses accounts for a good many facts because devised for that purpose; but there is as yet no independent proof. According to this point of view there is no necessary relation between overvoltage and catalytic activity. The first depends upon the slowness with which equilibrium is reached and the second on the point at which equilibrium is reached, two entirely different things.

Experiments by Rupert and by Willstätter and Waldschmidt-Leitz indicate that hydrogenation by means of platinum takes place better—perhaps only—in presence of oxygen. No adequate explanation has yet been offered for this phenomenon.

* * *

It has seemed that the best thing the committee could do in its first report was to outline the present situation in regard to contact catalysis as clearly as possible. After that, it should be a relatively simple matter for the committee to determine what to do next.

Definite Intermediate Compounds

There are two apparently distinct types of contact catalysis, one in which a definite chemical compound is formed, and the other when we have adsorption with activation. We will take up first the case in which definite chemical compounds are formed. In the catalysis of hydrogen peroxide by mercury, the intermediate formation of mercuric peroxide can be detected by the eye because there is an intermittent formation of a film[2] which then breaks down, only to form again. This periodic phenomenon represents an extreme case. Under ordinary conditions the formation and decomposition of the intermediate compound take place almost simultaneously, and of course at equal rates when a "steady state" is reached. In this dynamic equilibrium the quantity of the intermediate substance remains constant under constant experimental conditions. The dynamic equilibrium may also be considered as a limiting case of periodicity, the length of the period being practically zero and the number of periods per unit time very great.

Visible evidence of intermediate compound formation in contact catalysis is also obtainable in the oxidation or dehydrogenation of methanol in the presence of air and metallic copper. The copper gauze varies in color, showing constant changes in the state of oxidation.

Bayley[3] states that cobalt is oxidized by hydrogen peroxide and that this reacts with hydrogen peroxide, oxygen being evolved from both and the cobalt going back to a lower oxide. This is then oxidized to cobalt peroxide and the same series of changes is continued. Oxide of cobalt therefore decomposes hydrogen peroxide catalytically. When cobalt oxide decomposes hypochlorites catalytically, Bayley considers that the cobalt oscillates between Co_3O_5 and CoO_2. He says that Co_3O_5 has been shown to be the final product but he gives no reference. Hydrogen peroxide does not oxidize nickel oxide to a peroxide and is therefore not decomposed catalytically by it.[4] If nickel peroxide is made independently, it reacts with hydrogen peroxide just as the corresponding cobalt salt does. These experiments seem to prove fairly conclusively that one stage in the catalytic decomposition of hydrogen peroxide by cobalt oxide is the formation of cobalt peroxide. It would be interesting to see whether a change of temperature or of some other factor would make the oxide of nickel behave like the oxide of cobalt, or vice versa. Hydrated ferric oxide and hydrated zinc oxide do not react with hydrogen peroxide, and consequently Bayley does not consider them as peroxides. It would be interesting to know the action of hydrogen peroxide on passive iron.

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[1] Report of Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by the chairman in collaboration with the other members of the committee: Messrs. H. Adkins, W. C. Bray, R. F. Chambers, C. G. Fink, E. P. Kohler, A. B. Lamb, E. E. Reid, and H. S. Taylor. Received February 4, 1922.

[2] Bredig and von Antropoff, *Z. Elektrochem.*, **12** (1906), 581; von Antropoff, *J. prakt. Chem.*, [2] **77** (1908), 273.

[3] *Phil. Mag.*, [5] **7** (1879), 126.

In the catalytic oxidation of carbon monoxide by mixed oxides of cobalt, manganese, etc., it is usually believed that there is alternate (or simultaneous) reduction and oxidation of the catalyst. The oxygen carrier oxidizes the carbon monoxide and is itself reoxidized by the oxygen of the air. While this is undoubtedly the case, no measurements have yet been published, showing the two end stages between which the catalyst oscillates.[5] This is known, however, for the case of the catalytic oxidation of alcohol by air in presence of osmium tetroxide[6] because this reaction can be run in two stages. Osmium tetroxide will oxidize alcohol in the absence of air, and air will oxidize the dioxide to the tetroxide. When carbon monoxide is activated by metallic copper in an alkaline solution, Hofmann[7] considers that there is intermediate formation of Cu_2O_3 or CuO_2.

Armstrong and Hilditch[8] consider that the catalytic action of ferro-ferric oxide on carbon monoxide and water is due to the alternate reduction of the ferro-ferric oxide to ferrous oxide or iron by the carbon monoxide, and oxidation of these compounds by water. The acceleration of the reverse reaction by ferro-ferric oxide can be accounted for in a similar manner, reduction by hydrogen and oxidation by carbon dioxide. At a suitable temperature the iron oxide causes the reaction to proceed practically to equilibrium. Metallic copper accelerates the reaction between carbon dioxide and hydrogen; but even at its optimum temperature does not cause more than 50 to 70 per cent of the possible amount of chemical change. Armstrong and Hilditch account for this on the assumption that copper tends to produce an equilibrium,

$$CO + H_2O \rightleftharpoons HCO_2H.$$

The formation of graphite is usually preceded by the formation of a carbide. The conversion of acetic acid into acetone[9] by passing the vapor over heated barium carbonate presumably involves the intermediate formation of barium acetate. In the Deacon chlorine process, where a mixture of hydrochloric acid and oxygen is passed over heated cupric chloride, Hurter[10] assumes the existence of an intermediate compound and he is probably right in this. People are not agreed, however, whether the intermediate compound is cuprous chloride, basic cupric chloride, or both.[11] The reaction as usually written is:

$$4CuCl_2 = 2Cu_2Cl_2 + 2Cl_2$$
$$2Cu_2Cl_2 + 4HCl + O_2 = 4CuCl_2 + 2H_2O$$

Since it is not probable that the second reaction takes place in one stage, we may write:

$$4CuCl_2 = 2Cu_2Cl_2 + 2Cl_2$$
$$2Cu_2Cl_2 + O_2 = 2CuO.CuCl_2$$
$$2CuO.CuCl_2 + 4HCl = 4CuCl_2 + 2H_2O$$

There seems to be no evidence that cupric chloride breaks down into cuprous chloride and chlorine at the temperature employed, so we have another formulation:

$$4CuCl_2 + O_2 = 2CuO.CuCl_2 + 2Cl_2$$
$$2CuO.CuCl_2 + 4HCl = 4CuCl_2 + 2H_2O$$

This seems more reasonable than the others; but we do not know whether this, or any, basic cupric chloride is formed. If we start with copper sulfate as catalytic agent, which may be done, the whole thing becomes hopelessly complicated. There is really no definite knowledge in regard to the intermediate compound or compounds at all.

Mr. Bray points out that this alternative suggestion, that oxygen can displace chlorine from solid cupric chloride, may be considered as a border-line case. In a crystal of cupric chloride the cupric chloride "molecules" are combined with each other. A single oxygen molecule might be taken up and two molecules of chlorine be given off without the formation of a definite new molecule, such as the basic cupric chloride suggested. On the other hand, as anhydrous copper sulfate is really a good catalyst the mechanism may be that hydrochloric acid molecules are taken up by the copper salt (chloride or sulfate) and that the oxygen then attacks the hydrogen of the added hydrochloric acid, setting free chlorine. Mr. Bray endorses the statement that there is as yet no real evidence of the formation of a definite intermediate compound. Mr. Taylor writes that he does not now think that the Deacon chlorine process involves intermediate compounds at all. He expects that experiments now being prepared at Princeton will show that the copper halides probably adsorb hydrochloric acid gas and sulfur dioxide—possibly oxygen.

This indefiniteness in regard to the nature of the intermediate compound is a serious defect in much of the work on contact catalysis. Sabatier[12] believes that the catalytic action of alumina on alcohol is due to the intermediate formation of an instable compound of alumina and water, while Henderson[13] assumes the intermediate formation of aluminium ethylate. Neither man offers any experimental evidence in support of his belief, and neither one discusses why kaolin should act practically as well as alumina. The formation of a definite kaolin ethylate seems improbable. Sabatier assumes definitely the existence of intermediate compounds of metal and hydrogen in hydrogenation and dehydrogenation processes. He says:

> This conception of the way in which catalytic action occurs [temporary formation of intermediate compounds] is supported by the experimental confirmation of the predictions which one can make. If the metallic catalytic agents, nickel, copper, etc., tend to react with hydrogen, forming intermediate products analogous to the hydrides, these metals must also be able to remove hydrogen from substances which can give off hydrogen. In other words, these metals should act also as dehydrogenating catalysts. It was this line of thought which caused Sabatier and Senderens to try these metals as catalyzers for the dehydrogenation of alcohols into hydrogen and aldehydes or ketones. It was found that nickel was less suitable than copper for this purpose because of its tendency to form with carbon monoxide an intermediate compound which was instable at the temperature of the reaction and which gave rise to a secondary decomposition of the aldehydes and ketones.

This seems to satisfy the scientific criteria. The hypothesis is used to predict new results and the new results are obtained. The experiments of Taylor and Burns,[14] however, show that no compounds analogous to the hydrides are formed with nickel and copper.[15] The flaw in Sabatier's reasoning is that he did not consider the possibility of some other hypothesis leading to the same conclusion.

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[4] Work done at Cornell since this report was written indicates that Bayley is wrong in this statement. The whole subject is now being studied.

[5] Mr. Bray believes that it is useless to try to decide whether, at the dynamic equilibrium, a molecule of oxygen at the surface of the catalyst actually changes some of a lower oxide to a higher (and the reverse change with carbon monoxide) or whether the oxygen is merely held on the surface in an active condition ready to combine with carbon monoxide. In either case all the processes are taking place simultaneously.

[6] Hofmann, *Ber.*, **45** (1912), 3329; **46** (1913), 1657, 2854; **46** (1915), 1585.

[7] *Ber.*, **51** (1918), 1334, 1526; **53B** (1920), 2165.

[8] *Proc. Roy. Soc. London*, **97A** (1920), 266.

[9] Squibb, *J. Am. Chem. Soc.*, **17** (1895), 187.

[10] *J. Soc. Chem. Ind.*, **2** (1883), 106.

[11] Woker, "Die Katalyse," **1910**, 474.

[12] "Die Katalyse in der organischen Chemie," **1914**, 240.

[13] "Catalysis in Industrial Chemistry," **1919**, 4.

[14] *J. Am. Chem. Soc.*, **43** (1921), 1273.

[15] Mr. Bray considers that the "tendency" of a metal like nickel to combine with hydrogen may exist even when a definite compound does not form. He believes that this is the correct explanation of adsorption at higher temperatures.

Armstrong and Hilditch[16] believe that catalytic change is always effected by the intermediate formation of definite chemical compounds, although they do not postulate in general the formation of intermediate compounds of well-defined stability. They consider that these are not to be expected in the course of catalytic change, the specific action of various catalysts probably depending largely on the suitable instability of the intermediate complex for the purposes of the action—in other words, the change of the compounds which they have studied depends on the coincidence that the catalyst and the initial substance will interact to form a compound sufficiently instable under the conditions prevailing to decompose (or interact with other constituents of the system), giving new products.

Armstrong and Hilditch say, in regard to these intermediate compounds that

> The physicochemical data from which our present deductions are made do not afford any evidence as to the precise stoichiometrical relation, subsisting between catalyst and organic compound. The latter is not necessarily simple, for example, an atom of nickel in temporary union with an organic group containing one ethylenic linkage: it may be more probably of the nature of a "coördinated" compound comparable to nickel carbonyl, in which the "subsidiary valences" of the interactants play the chief part; or again, the combination might be still less definite and analogous to the adsorption of dye by fibers, in which case the composition of the unstable complex might vary with physical conditions such as temperature or concentration. By "intermediate compound" in the present series of papers we mean an association between catalyst and the other compounds due to the same "chemical" forces which operate in more ordinary chemical actions, but we are not able to offer any opinion as to the precise character of the compounds thus transiently produced.

In an earlier paper the study of the hydrogenation of liquid fats in presence of nickel led Armstrong and Hilditch[17] to believe that there is formed a ternary, unspecified, and instable complex of nickel, unsaturated fat, and hydrogen, which breaks down into a saturated, or more saturated, fat and nickel. The nickel is believed to attach itself in some way to the unsaturated carbons, —CH : CH—. They also consider that the interchanges take place in an electrolytic circuit in which the interacting substances are necessarily all comprised. The hydrogen and the fatty oil are both to be thought of as coupled with the nickel and the interaction as brought about through the inclusion in the system of the electrolyte required to establish a conducting circuit. Both hydrogen and the fatty oil are to be regarded as having some affinity for the catalyst; and the rate of change is to be considered as determined by the rate at which the less active hydrogen enters into productive association with the catalyst.

Dehydrogenation is believed to be due to the reverse formation of the nickel—unsaturated compound—hydrogen complex. In the partial hydrogenation of ethyl oleate, ethyl stearate is formed[18] and also ethyl esters of isomeric forms of ordinary oleic acid, these being most probably ethyl elaidate and an ethyl "iso-oleate" derived from $\Delta^{11:12}$ oleic acid. The appearance of the elaidic ester, the stereoisomeric form of ordinary oleic ester, is readily explained by the assumed equilibrated action between the catalytic nickel and the ethylenic linkage, for on re-formation of the constituents during the balanced action it is plain that either or both stereoisomeric ethylenic derivatives might result. The production of the isomeric form of oleic acid takes place to a greater extent the higher the temperature of hydrogenation, and is also more marked at equal temperatures, with palladium, generally a more vigorous catalyst than nickel.

Though Armstrong and Hilditch believe firmly in the formation of definite intermediate compounds, their conception of an intermediate compound is so elastic and their knowledge of the compositions of the assumed intermediate compounds is so limited, that there would probably be no difficulty in rewriting all their results in terms of adsorption.

INDEFINITE INTERMEDIATE COMPOUNDS

While there are undoubtedly many cases of contact catalysis involving the formation of definite intermediate compounds, it is equally certain now that many others do not come under this head. Mention has already been made that no hydrides of nickel and copper are formed under the conditions favorable to catalytic action. It seems improbable that it would be so difficult to make carbon tetrachloride if the chlorine which is adsorbed by charcoal[19] and thereby made active consisted of a compound of carbon and chlorine. Oxygen adsorbed by charcoal will oxidize ethyl alcohol to acetic acid[20] and ethylene to carbon dioxide and water, reactions which are certainly not due to any known oxide of carbon. It is very important that we should decide in each given case whether a definite intermediate compound is formed and, if so, what compound. Only in this way can we escape from the haziness which mars so much of the work on catalysis.

The view of Armstrong and Hilditch is practically the same as that of Mr. Bray, except that he prefers to speak of indefinite chemical compounds instead of definite ones and he considers these indefinite compounds as identical with adsorbed material wherever adsorption is something more than capillary condensation. While he agrees with the statement that the results of Armstrong and Hilditch could be rewritten in terms of adsorption, he would prefer to translate many results now expressed in terms of adsorption back into the language of indefinite compounds. Mr. Bray would like to see emphasized the differences between what he calls the two classes of adsorption: (1) when the amount of material adsorbed is relatively small and not more than one molecule in thickness; and (2) when the adsorption takes place on a porous material at a relatively low temperature, in which case capillary forces come into play and a relatively large amount of material is adsorbed.

He believes that it will be difficult at times to distinguish between definite and indefinite compounds. When we are not dealing with contact catalysis, it is usually easy to decide whether or not two substances, A and B, react to form a definite compound. Thus oxygen will react with solid calcium to form a definite oxide but not with platinum or with carbon at relatively low temperature. If it were not possible to bring more than a few molecules of oxygen to the surface of one of these elements, Mr. Bray believes "that it would be almost impossible to decide whether or not a definite compound is formed. A single atom of oxygen on a surface of calcium or platinum would be held by the same kind of bond (or valence force) in the two cases and it is only after the introduction of much more oxygen that the difference appears. The molecules of the definite compound calcium oxide arrange themselves as required in that compound, and we may say that the Ca-Ca bonds are broken. On the other hand, Pt-Pt or C-C bonds are not broken and the action of the oxygen is restricted to the surface. In the latter case we have adsorption."

There are two points on which Mr. Bray lays no stress. It is of course possible that oxygen may be adsorbed to a varying extent as molecular oxygen without necessarily forming a substance analogous to a peroxide because it may be held by different bonds or contravalences. When the Pt-Pt or C-C bonds are broken, as in the formation of a definite chemical compound, we get two phases, each of constant composition, in case the definite compound is a solid. In the corresponding case of the indefinite compound, the system behaves like a phase of continuously varying concentration.

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[16] *Proc. Roy. Soc. London*, **98A** (1920), 37.

[17] *Ibid.*, **96A** (1919), 137, 322.

[18] Moore, *J. Soc. Chem. Ind.*, **38** (1919), 320.

[19] Damoiseau, *Compt. rend.*, **73** (1876), 60.

[20] Calvert, *J. Chem. Soc.*, **20** (1867), 293.

Waiving these two points, there is substantial agreement between the viewpoint from which the bulk of the report is written and that held by Mr. Bray. The difference is in the stress laid on different sides of the problem. It is admitted that we may have definite compounds, indefinite compounds, and capillary condensation. Mr. Bray wishes to emphasize the difference between the last two, perhaps because of the differences between adsorption by carbon and adsorption by silica. For reasons to be given in the next few paragraphs, the chairman of the committee feels that the capillary condensation plays so small a part in the interesting cases of contact catalysis that it may be neglected, especially since the theory of it presents no difficulties. On the other hand the failure to distinguish as sharply as possible between definite and indefinite intermediate compounds has apparently been one of the reasons for the retarded development of a theory of contact catalysis. It is in order to emphasize this distinction that the term "adsorption" has been used in many cases in preference to the term "indefinite compound." The difference is psychological and not chemical.

In so far as the reaction takes place in or at the surface of the catalytic agent without formation of definite intermediate compounds we are dealing with adsorption and we must now consider the general case of adsorption with activation or activation in consequence of adsorption.

ACTIVATION

Since reaction velocity is a function of the concentration of the reacting substances, it was natural to ascribe the catalysis of oxyhydrogen gas by platinum to the increased concentration. We know now that this is not the whole truth, because it was found during the war that oxyhydrogen gas was quite stable under pressures of two thousand atmospheres. This shows that the catalytic action of platinum black is due to something more than an increase in concentration. The marked difference in the behavior of platinum and charcoal towards oxyhydrogen gas is another argument in favor of the action of a catalytic agent being specific. Patrick's silica gel has a surface of 2.5×10^6 sq. cm. per gram and is an excellent adsorbent; but it does not catalyze many reactions which are accelerated by platinum or charcoal.[21] It does, however, accelerate the reaction between nitric oxide and oxygen; and it is very effective in the synthesis of amines. The prediction was made[22] that it would work well with the mixed vapors of alcohol and acetic acid at 100° because this reaction takes place at a measurable rate in the vapor phase in the absence of any catalyst and consequently the effect of increased concentration should be extremely marked. This prediction has been verified by Reid at the Johns Hopkins University; but there is apparently a specific effect because Reid obtained a 76 per cent yield of ethyl acetate over quite a long period of time, although the theoretical equilibrium corresponds to 67 per cent conversion.

Increased concentration at the surface of the catalytic agent cannot, of course, account for cases in which a substance decomposes in one way in the presence of one catalytic agent and in another way in the presence of a second. A typical case of this is the breaking down of alcohol into ethylene and water in presence of alumina and into acetaldehyde and hydrogen in presence of pulverulent metals. Senderens[23] finds that amyl alcohol gives varying dehydration products with varying age of the same catalytic agent. This certainly is not exclusively a concentration effect.

W. C. McC. Lewis[24] believes that all catalysis is due to infra-red radiation, and a similar view has been put forward by Perrin.[25] Rideal[26] has come out in favor of this view and it has been criticized severely by Langmuir,[27] with a rebuttal by Lewis.[28]

It apparently is not claimed that these infra-red radiations act effectively at finite distances. It is believed that they act only on adsorbed material. Even with this limitation the hypothesis has difficulties before it. Zsigmondy[29] showed years ago that alumina and salts of aluminium do not absorb infra-red rays. This means that they do not emit these rays and that consequently alumina should be a very bad catalytic agent, whereas it is an admirable one for some purposes. Of course it is possible that alumina absorbs infra-red rays very strongly at the temperatures at which it is effective catalytically; but that should have been shown in advance by the proponents of this hypothesis. It seems scarcely possible that the absorption of infra-red radiation by the reacting substance at the surface of the catalyst can vary in nature with the state of subdivision of the catalyst at a given temperature. It is therefore difficult to see how, on this hypothesis, the dehydration products of amyl alcohol[33] can vary with the age of the catalytic agent. It is perhaps unreasonable to insist upon it; but one would really like to know which lines or bands in the infra-red give rise to the different products which are obtained when ethyl acetate, for instance, is passed over different catalytic agents.

Tyndall[30] has pointed out that gum arabic is exceedingly opaque to the infra-red rays. According to the hypothesis, addition of gum arabic to a solution of methyl acetate ought to be at least as effective in promoting hydrolysis as adding hydrochloric acid. Somebody will certainly have to try this experiment. It is quite extraordinary that a theory like this should get a scientific standing with apparently nothing back of it.

If we eliminate radiation, the only remaining possibilities seem to be that we may have more effective collisions between molecules or that we may have the conversion of one or more of the reacting substances into an active form.

According to the kinetic theory the reaction velocity is proportional to the number of collisions between possibly reacting molecules; but it does not follow at all that two molecules react every time they collide. If a large number of collisions is necessary on an average before a pair of molecules react, anything which would make these collisions more helpful might increase the reaction velocity enormously. The first question is then whether there is any evidence of ineffective collisions. This matter has been studied by Strutt,[31] who comes to the conclusion that a molecule of ozone reacts every time it strikes a molecule of silver oxide; but that a molecule of active nitrogen collides with a molecule of copper oxide five hundred times on an average before they react, while two molecules of ozone at 100° collide on an average 6×10 times before they react. Without insisting on the absolute accuracy of these figures, there is evidently plenty of margin for an increase in reaction velocity with ozone at 100° if one could produce more effective collisions. Langmuir[32] finds that 15 per cent of all oxygen molecules at a pressure of not over 5 bars striking a tungsten filament at 2770° K. react with it to form tungstic oxide, WO_3. This coefficient increases at higher temperatures, and at 3300° K. about 50 per cent of all the oxygen molecules which strike the filament react with it to form WO_3. Since there are three atoms of oxygen in WO_3 and only two in the oxygen molecule, Langmuir considers that at least one-half of the tungsten surface must be covered at 3300° K. with oxygen in some form.

It is possible that a catalytic agent may cause one molecule to strike another amidships instead of head-on and may thereby increase the effectiveness of the collisions. It is not impossible that part at least of the effect of solvents on reaction velocity may be due to some such thing as this. If we adopt Langmuir's views of oriented adsorption, all sorts of things become possible. If ethyl acetate, for instance, attaches itself to one adsorbent by the methyl group, to another by the ethyl group, and to a third by the carboxyl group, it might very well be that bombardment of the captive molecule by free ones might lead to very different reaction products in the three cases. Such a suggestion is of very little value, however, unless it can be made definite. We do not know as yet whether ethyl acetate is actually adsorbed in one way by nickel, in another way by thoria, and in a third way by titania, nor do we know whether the difference in the manner of adsorption, assuming it to occur, is of such a nature as to account for the differences in the reaction products. It may well be that some entirely different hypothesis will prove necessary. The general problem of increasing the effectiveness of molecular collisions is distinctly an important one which has not been studied at all.

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[21] Taylor, *Trans. Am. Electrochem. Soc.*, **36** (1919), 150.

[22] Bancroft, *Ibid.*, **37** (1920), 31.

[23] *Compt. rend.*, **171** (1920), 916.

[24] *J. Chem. Soc.*, **105** (1914), 2330; **107** (1915), 233; **109** (1916), 55, 67, 796; **111** (1917), 457, 1086; **113** (1918), 471; **117** (1920), 623; "System of Physical Chemistry," **5** (1919), 138.

[25] *Ann. phys.*, [9] **11** (1919), 5.

[26] *Trans. Am. Electrochem. Soc.*, **36** (1919), 195; *J. Chem. Soc.*, **117** (1920), 1288. Criticized by Taylor, THIS JOURNAL, **13** (1921), 75.

[27] *J. Am. Chem. Soc.*, **42** (1920), 2190.

[28] *Ibid.*, **43** (1921), 75.

[29] *Dingler's polytech. J.*, **37** (1893), 17.

[30] "Fragments of Science: Radiant Heat and Its Relations."

[31] *Proc. Roy. Soc. London*, **87A** (1912), 302.

[32] *J. Am. Chem. Soc.*, **35** (1913), 105; **38** (1916), 2270.

Instead of more effective collisions between unchanged portions of the reacting molecules, we may have a partial conversion of one or more of the reacting substances into active forms either through the rupture of normal valences or of contravalences, opening up fields of force, as Baly[33] puts it.

In order to account for the change of reaction velocity with change of temperature in the case of such reactions as the inversion of cane sugar, Arrhenius[34] fell back on the hypothesis which had developed into the electrolytic dissociation theory and postulated the existence of active and inactive molecules of cane sugar. If the number of active molecules is very small relative to the inactive ones, a slight displacement of the equilibrium will account for a large percentage increase in the reaction velocity. This hypothesis did not prove fruitful and no progress was made in determining what was the difference between the active and inactive molecules. Since the majority of reactions have temperature coefficients larger than can be accounted for on the kinetic theory, this meant that practically all substances occurred in two forms, the active form always being relatively low in concentration. This was so unsatisfactory that most persons have preferred to accept the temperature coefficient as an empirical fact without attempting any theoretical explanation.

Baly and Krulla[35] consider that the change to an active form consists in opening the condensed systems of force lines.

> Although the term residual affinity has frequently been used to explain many chemical processes, no satisfactory and connected explanation has been brought forward as to the nature and origin of this property. It is generally accepted that the formation of compounds such as hydrates and double salts are due to the secondary valencies of the atoms of the compounds concerned, and that every elementary atom possesses these secondary valencies to a greater or lesser extent. In any compound that is formed by virtue of the primary valencies of its atoms only, the secondary valencies are unsaturated. Every atom must therefore be the center of a field of force, the nature and strength of which depends on the nature of the secondary valencies in each case. In addition to the unsaturation of the secondary valencies, we must add the unsaturation of the primary valencies, when this is known to exist. Clearly therefore such atoms in a compound must be the center of a field of force, the lines of which radiate in every direction.
>
> Now the independent existence of the several fields of force in any one molecule must be a metastable condition, for the line of force of the several fields must condense together with the escape of free energy. The results of this condensation will be the production of a closed system of force lines, and the free affinities of the molecule will be considerably reduced. When the condensation of the force lines has occurred, it is not necessary that the whole of the free affinities should disappear, for this will only take place when there is a perfect equality between those of opposite type within the molecule. In those cases where there is not a perfect equality there will naturally be left a balance of affinity, and it is this balance which should be defined by the term "residual affinity," and this term should mean that amount of affinity left uncompensated after the maximum condensation between the force fields has occurred. This residual affinity of a molecule may be of positive or negative, or, as more usually called, basic or acid type, according to the conditions obtaining within the molecule.
>
> Again it is evident that the chemical activity of a molecule must depend on the free affinity which exists, and it is a necessary deduction that the condensing together of the lines of force must result in a decrease of chemical reactivity, and, indeed, it would seem to follow that the true chemical affinity of any molecule cannot be exhibited until the condensed systems of force lines within each molecule have been unlocked or opened by some means.

Baly and Rice[36] have applied this conception of condensed systems of force lines around the molecules to chemical action and to catalysis.

> It is evident that the condensing together of the lines due to the force fields round the component atoms of a molecule must result in an enormous decrease in the reactivity of the molecule, and, in fact, it may be said that such a condensed system cannot react unless it previously be opened or unlocked by some means. For example, the well-known cases described by Baker, when pure, dry substances, such as ammonia and hydrogen chloride, lime and carbon dioxide, do not react together are doubtless due to the fact that the force fields of the molecules are so condensed together that no reaction takes place when they are brought together. The presence of water is required in order to open these systems sufficiently for the reaction to proceed, the merest trace of water being enough to catalyze the whole reaction. Again, the converse cases of the vapors of ammonium chloride and mercurous chloride may be explained in the same way, for these molecules evidently possess their force fields so condensed that increase of temperature alone is not sufficient to open them, and the vapor densities correspond with those of the undissociated molecules. The presence of water, however, opens the condensed fields sufficiently for the molecules to dissociate under the influence of higher temperatures.
>
> The general phenomenon of catalysis is capable of explanation on these lines, for a catalytic agent may be defined as one which opens the condensed system of the reacting substance or substances so that their chemical reactivity is enhanced. Negative catalysis is equally capable of explanation, for a negative catalyst is simply a type of substance which tends to close up the condensed systems, and thus conteract the action of the solvent. Specific evidences of such closing of the molecular systems have been observed from absorption spectra, as will again be mentioned.
>
> It follows from the above that any chemical reaction must take place in at least two stages. First, the reacting substances must have their condensed systems opened up, and, secondly, these opened systems will react together to give the expected compound. It is clear that these stages should be possible of observation, and that, in the event of their taking place, they should evidence themselves in some way. There is no doubt that the explanation of the color changes of the aromatic aminoaldehydes and ketones when treated with alcoholic hydrogen chloride are due to these stages in the reaction. When, for example, *o*-aminobenzaldehyde is dissolved in alcohol, the condensed system is partly opened, owing to its penetration by the force lines due to the residual affinity of the alcohol. On the addition of hydrogen chloride, the final product is, of course, the hydrochloride; but the base in the form in which it exists in alcoholic solution does not itself react with the acid to give the salt. It passes through an intermediate phase when it is opened up to a more complete stage, and it is this intermediate phase that reacts with more acid to form the salt. The intermediate phase has a yellow or red color with a characteristic absorption band[37] as has already been described.

Experiments with the nitroanisols dissolved in alcohol and in concentrated sulfuric acid showed the occurrence of a stage in the sulfuric acid solution preliminary to the sulfonation. The authors consider that this is an intermediate formation of $CH_3OC_6H_5.H_2SO_4$. They consider that any molecular transformation whatsoever may be looked upon simply as a rearrangement of the electrons due to the potential gradient within the condensed systems of force lines of the molecule being sufficiently steep.

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[33] *J. Chem. Soc.*, **101** (1912), 1469, 1475.

[34] *Z. physik. Chem.*, **4** (1889), 226.

[35] *J. Chem. Soc.*, **101** (1912), 1469.

[36] *J. Chem. Soc.*, **101** (1912), 1475.

[37] Baly and Marsden, *J. Chem. Soc.*, **93** (1908), 2108.

In a discussion of catalysis in homogeneous systems, Dhar[38] says: "If active and inactive molecules exist, it appears reasonable to expect that a catalyst or light simply acts in shifting this equilibrium. Plainly if sufficient catalyst were added to change a relatively large amount of inactive into active molecules or vice versa, it would follow that the temperature coefficient would be smaller than when the reaction is not catalyzed." This proved to be true experimentally.[39] In the oxidation of quinine sulfate by chromic acid, the temperature coefficient is 1.87 in the dark and 1.04 in the light. With iodine and potassium oxalate, the temperature coefficient is 6.73 in the dark and 3.4 in diffused light. Mercuric chloride and potassium oxalate showed a temperature coefficient of 2.2 in the dark and 1.19 in the light.

The conception of Baly that a catalytic agent activates the reacting substances by opening up fields of force covers the ground admirably as a purely formal statement. The trouble is that it is as yet too vague to be of any value as a working hypothesis, though it is undoubtedly the best starting point. By combining Baly's hypothesis with a modified form of Langmuir's theory of adsorption, we may get something really worth while.

Langmuir considers that the particles of a crystal of any solid mass are held together by chemical forces and therefore constitute a giant molecule. An adsorbed gas will be held chemically by the unsaturated valences at the surface of the solid. He says:

> In general the law of multiple combining proportions will apply. Thus each metal atom of the surface will be capable of holding a definite integral number (such as one or two of atoms of the gas or possibly each two atoms of metal may hold one atom of gas). The atoms held on the surface in this way will form a part of the solid body, being a real continuation of the space lattice of the solid. This layer of atoms (or molecules) on the surface may be said to be adsorbed. The surface of the metal is thus looked upon as a sort of checker-board containing a definite number, N_0, of spaces per square centimeter. The number of elementary spaces, N_0, is probably usually equal to the number of metal atoms on the surface. But this is not essential, for we can imagine cases in which each atom holds, for example, two adsorbed atoms or molecules, so that we should then have twice as many elementary spaces as metal atoms on the surface.

These so-called compounds are not of the ordinary type and no definite formulas can be written for them. In the case of the adsorption of argon by charcoal, we should have to write C_xAr_y where x varies with the mass of charcoal and y with its surface and also with the pressure and temperature. These substances should therefore be called indefinite intermediate compounds.

Starting from this point of view, Langmuir[40] has developed a theory of contact catalysis, which however deals primarily with the form of the reaction velocity equations and does not throw much light on the real problem of contact catalysis. This defect could be remedied if the theory were developed to such an extent as to show that an ester was adsorbed in different ways by different catalytic agents and that the reaction took place at the point of the molecule where the ester tied on to the adsorbent, forming the indefinite compound. This is a perfectly normal development because Langmuir now postulates that hydrogen is taken up—or at least is given off—as monatomic and not as molecular hydrogen.

PROMOTERS

This general treatment of contact catalysis as a problem in activation has the advantage of suggesting a possible explanation for the behavior of promoters. Rideal and Taylor[41] say:

> Thus far no theory put forward to account for the acceleration of reaction by minute quantities of promoters added to the main catalyst is completely satisfactory. A possible mechanism, which, however, has received no experimental test, may be advanced by considering the case of ammonia synthesis from mixtures of nitrogen and hydrogen. Reduced iron is an available contact substance, the activity of which may be regarded as due to the simultaneous formation of the compounds, hydride and nitride, with subsequent rearrangement to give ammonia and unchanged iron. Or, maybe, the activity of the iron is due to simultaneous adsorption of the two gases. The particular mechanism of the catalysis is unimportant for the present considerations. Now such bodies as molybdenum, tungsten, and uranium have been proposed, among others, as promoters of the activity of iron. It is conceivable that these act by adjusting the ratio in which the elementary gases are adsorbed by or temporarily combined with the catalytic material to give a ratio of reactive nitrogen and hydrogen more nearly that required for the synthesis, namely, one of nitrogen to three of hydrogen. From the nature of the materials suggested as promoters, it would seem that they are in the main nitride-forming materials,[42] which on the above assumption of mechanism would lead to the conclusion that the original iron tended to adsorb or form an intermediate compound with a greater proportion of hydrogen to nitrogen than required by the stoichiometric ratio. The catalytic activity of reduced iron as a hydrogenation agent would tend to confirm this viewpoint.
>
> In reference to this suggested mechanism it must be emphasized, however, that in such examples of "promotion" as require only minute quantities of added promoter the activity is more difficult to understand. With the case of the ammonia synthesis, the promoters are added in marked concentrations. It is difficult to realize, however, that 0.5 per cent of ceria or a concentration of one molecule of ceria among two hundred molecules of iron oxide, in the example cited above in reference to catalytic hydrogen production, can so far "redress the balance" of adsorption or combination as to produce the marked increases in activity of which it is capable. It is obvious that in this phase of the problem there lies an exceedingly fascinating field for scientific investigation, with the added advantages that, being practically virgin territory, the harvest to be gained therefrom should be rich and abundant.

Instead of the promoter changing the ratio of adsorption, it may be that the catalytic agent activates only one of the reacting agents or activates one chiefly, and that the promoter activates the other. Thus it may be, in the ammonia synthesis, that iron activates the hydrogen chiefly so that we have hydrogenation of the nitrogen. The molybdenum may tend to activate the nitrogen giving rise to nitridation of hydrogen, or it may increase the activation of the nitrogen. Such a state of things is not impossible theoretically. When a dye reacts with oxygen under the influence of light, the light may make the oxygen active and the activated oxygen may oxidize the dye, or it may be that the light makes the dye active and that the activated dye reduces the oxygen. It is easy to decide this question by seeing whether the effective light corresponds to an absorption band for the dye or for the oxygen. In many cases it is the dye that is made active.[43]

(*To be continued*)

At the first meeting of the recently formed Interdepartmental Petroleum Specifications Committee, held in the offices of the Bureau of Mines in Washington, D. C., February 27, 1922, consideration was given to certain changes in specifications for lubricating oils of various grades, which were advocated by refiners on the Pacific Coast. Some of the changes suggested were agreed to by the Committee. The changes have been submitted to the Federal Specifications Board, and it is hoped to incorporate them in the technical paper containing revised specifications for petroleum products, to be published shortly by the Bureau of Mines.

The Committee postponed the discussion of proposed changes in specifications for transformer oil, aviation gasoline, kerosenes, and signal oil.

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[38] *J. Chem. Soc.*, **111** (1917), 746.

[39] Cf. Cox, *Ibid.*, **119** (1921), 142; Baly and Barker, *Ibid.*, **119** (1921), 653.

[40] *J. Am. Chem. Soc.*, **38** (1916), 2286.

[41] "Catalysis in Theory and Practice," **1919**, 31.

[42] The dissociation equilibrium of iron nitride has recently been studied by Noyes and Smith, *J. Am. Chem. Soc.*, **43** (1921), 475.

[43] Depierre and Clouet, *J. Soc. Dyers Colourists*, **1** (1885), 245; Dufton, *Ibid.*, **10** (1895), 92; Bredig and Pemsel, *Beibl.*, **23** (1899), 795.

Progress in Metric Standardization[1]

By **Eugene C. Bingham**

Chairman, Metric Committee, American Chemical Society

OUR report in the October issue of THIS JOURNAL showed that out of 195 universities heard from to date, 194 were ready to change current practice in order to gain the advantages of metric standard packages. This was so nearly a "quantitative yield" that it was feared that those opposing the movement were refraining from expression; so a letter was sent out asking all to reply *even if opposed* to the SOCIETY's proposal. As a result, over a hundred additional colleges have been heard from, *without a single dissenting voice*. The colleges remaining to be heard from certainly constitute a minority of the American colleges and it is not probable that *they* are all opposed to our proposal. If it can be established that practically all of the colleges and universities in America are buying their chemicals in metric units as a part of a general campaign for the adoption of the metric system it should have great weight, for the universities are recognized leaders of thought.

The committee had been warned that those favoring the metric system were "crank professors" and that "practical men" were thoroughly opposed to it. Feeling that this opposition was greatly overestimated the committee has begun a canvass of certain firms who are supposed to be purchasers of pure chemicals. The replies are still coming in, but of the 300 received to date 6 are frankly opposed, 16 are not interested, having gone out of business, or being non-purchasers of pure chemicals, etc. This leaves 268 (Table I) who are heartily in favor of our proposal so that they are willing to change their method of buying pure chemicals and apparatus so far as may be necessary to meet our suggestion. Of the total, then, those frankly opposed number less than 3 per cent. With this start it seems probable that the great majority of the business firms of the country buying pure chemicals will line up with us, which is as gratifying as it is surprising in view of current opinion to the contrary.

Some of the firms opposing our proposal are very bitter, stating that the adoption of the metric system will cost amounts running into hundreds of thousands of dollars for each firm. Mr. Theodore H. Miller, of the De Laval Separator Co., states that his plant is now completely on a metric basis. The cost of the change does not even appear in the finished product. It did not cost as many hundreds of dollars as the hundreds of thousands prophesied. We believe that these people have been deliberately misinformed by those who say that with the adoption of the metric system even the plumbing in our houses will have to be changed. The gage of our railways, and even the couplings between the cars will, according to these misinformers, have to be altered. Because $16^1/_2$ in. do not come out an even number of centimeters, they would doubtless maintain that a man who wears a $16^1/_2$ collar would have to change his neck with the adoption of the metric system, quite oblivious of the fact that nature does not provide mankind with necks having dimensions in even half inches to suit a divinely instituted English system.

The opposing letters do not give any argument against the metric system except professing to be appalled at the cost. They forget the cost of *not* adopting it. Dr. Wolf states that it costs us unnecessarily a million years in a generation to educate our children in the English system. It costs us much in foreign trade and in inconvenience. One prominent engineer reports a cost to him personally of $10 per week by not having the metric system, because we specify particular gage numbers for different materials instead of specifying in mm. A No. 12 copper wire is not the same as a No. 12 iron wire, etc. The nations we trade with all use the metric system except the British Empire and *it* can hardly continue the present system when all the other nations use the metric system. World standardization promotes intercourse and understanding and, therefore, tends toward world peace. Would it not be well for our SOCIETY to join with other engineering societies and investigate carefully just how much it would cost to make the change? Take the chemical industry, for example. It was said by opponents of change that all our bottles and containers were blown in expensive molds, which could not be changed, to hold 4 oz., 8 oz., 16 oz., etc., and that they could not be used for metric packages. The facts known to every chemist are that chemicals differ in specific gravity, and 16 oz. of each chemical do not just fill a 16-oz. bottle. On the contrary, the bottles now in use are entirely suited to hold chemicals put up in standard packages. But if glass manufacturers started at any time to make 200-, 300-, 400-, 500-cc. bottles, etc., they would also be entirely satisfactory.

The facts may need reiteration, but they seem not to have escaped the notice of most American business men. A chief engineer writes:

> I am very much pleased to have your circular letter of November 28 indicating that at least some concrete effort is being made to put into practical operation the use of the metric system. I am an ardent supporter of this movement and am impatient to have the system put into general use in the country. However, I realize the senseless opposition in certain quarters and am glad to see any sort of beginning made, no matter how small, towards the adoption of the system. I will gladly see that all orders for chemical supplies are made in the metric system as far as this company is concerned.

From a highly successful glass maker we have, "We manufacture all of our chemical laboratory glassware to metric units, and shall in the future order our laboratory chemicals and apparatus as far as practicable in metric units."

The director of research of a powder company writes:

> I am pleased to have the opportunity of coöperating in the excellent work that the Metric System Committee is doing.
>
> While I have no authority to speak for the company, yet I can assure you that so far as our Research Department is concerned, we will endeavor to use metric quantities in our orders for laboratory chemicals, and I regard this as a perfectly rational step, in view of the fact that we use these chemicals entirely in metric quantities. The old system of buying a reagent by the pound and then weighing it out by the gram seems somewhat illogical, and I feel that we are taking a step in the right direction in now purchasing our laboratory chemicals in standard metric packages.
>
> The large number of companies and educational institutions which have already agreed to help in this work is an excellent augury of success. I have been greatly interested in noting the impetus which this movement has had since your committee started its work, and I wish to congratulate you on the excellent results achieved.

The president of a dyestuff works says:

> We are heartily in favor of the adoption of the metric system and, of course, like everybody else, we use it exclusively in what we may term internal work. We have not now and never did have an ounce or pound weight or scale in our research or checking laboratory. We quote prices on our products by pounds because we have to. We purchase by the pound, in most cases, because prices are so quoted, but we would willingly scrap all the beams and weights in the pound system from each and every set of scales in our place and purchase metric beams and weights if we could.

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[1] Received January 5, 1922.

TABLE I—LIST OF TECHNICAL FIRMS WHICH WILL HEREAFTER PURCHASE PURE CHEMICALS AND CHEMICAL SUPPLIES AS FAR AS PRACTICABLE IN METRIC UNITS (PRELIMINARY)

Aetna Portland Cement Co.
Agawam Chemical Works
Alameda Sugar Co.
Albert Pick & Co.
American Chemical & Mfg. Corp.
American Diamalt Co.
American Hard Rubber Co.
American Hominy Co.
American Lithographic Co.
American Magnesium Corp.
American Medical Products Co.
American Oak Leather Co.
American Pharmaceutical Co.
American Platinum Works
American Rubber & Tire Co.
American Steel & Wire Co.
Anaconda Lead Products Co.
Appleton Co.
Associated Oil Co.
Atlantic Chemical Works, Ltd.
Atlantic Refining Co.
Atlas Chemical Co.
Atlas Mineral Products Co.

Batavia Rubber Co.
Bausch & Lomb Optical Co.
Beacon Falls Rubber Shoe Co.
Beaver Board Companies
Beckett Paper Co.
Berger & Wirth
Bethlehem Foundry & Machine Co.
B. F. Goodrich Co.
Big Four Canning Co.
Bird-Archer Co.
Blue Ridge Talc Co.
Boal's Rolls Corp.
Bonner Portland Cement Co.
Bowker Insecticide Co.
Boydell Bros. White Lead & Color Co.
Brier Hill Steel Co.
Burmus Paper Co., Inc.
By-Products Coke Corp.

California Central Creameries
California Ink Co., Inc.
Canfield Oil Co.
Cape Girardeau Portland Cement Co.
Central Indiana Gas Co.
Cereal Products Co.
Charles F. Gledhill Co.
Chas. W. Young & Co.
Chateaugay Ore & Iron Co.
Chemical Pigments Corp.
Chemical Service Laboratories
Cheney Bros.
C. H. Stuart & Co.
Clinchfield Portland Cement Corp.
Coignet Chemical Products Co.
Columbia Graphophone Mfg. Co.
Condie-Bray Glass & Paint Co.
Congoleum Co., Inc.
Conkling-Armstrong Terra Cotta Co.
Continental Gin Co.
Converse Rubber Shoe Co.
Cornell Wood Products Co.
Corning Glass Works
Cosmos Chemical Co.
Crocker-McElwain Co.

Dayton Rubber Mfg. Co.
DeLorme-Holman Co.
Dewey & Almy Chemical Co.
Dexter Portland Cement Co.
Diamond Crystal Salt Co.
D. R. Sperry & Co.
Drueding Bros. Co.
Duriron Co., Inc.

E. & F. King & Co.
E. & G. Brooke Iron Co.
E. H. Sargent & Co.
Electro-Chemical Supply & Eng. Co.
Elijah Brauer & Co.
Elk Tanning Co.
E. L. Patch Co.
Elyria Enameled Products Co.
Emery Candle Co.
Emil Calman & Co.
Ernest Scott & Co.
Euston Process Co.

Fansteel Products Co.
Farwell Bleachery
Federal Glass Co.
Fibre Finishing Co.
Firestone-Apsley Rubber Co.
Fisk Rubber Co. (lab. supplies only)
Flash Chemical Co.
Ford Roofing Products Co.
Franco-American Chemical Works
French Battery & Carbon Co.

General Bakelite Co.
General Lead Batteries Co.
General Petroleum Corp.
Genesee Pure Food Co.
George A. Schmidt Co.
George J. Kelly, Inc.
George S. Mepham & Co.
Giant Portland Cement Co.
Gibbs Preserving Co.
Glens Falls Portland Cement Co.
Gorham Mfg. Co.
Graver Corp.
Griebel Instrument Co.

Hamersley Mfg. Co.
Harrison Mfg. Co.
Hercules Powder Co.
H. Heidenhain
Hiram Walker & Sons
H. J. Heinz Co.
Houston Cotton Oil Mill
Howe Rubber Corp.
H. O. Wilbur & Sons
Hudson Coal Co.
Huff Electrostatic Separator Co.
Hunnewell Soap Co.
Huron Portland Cement Co.
Hydraulic Pressed Steel Co.

Iliff-Bruff Chemical Co.
Independent Fisheries
India Refining Co.
Industrial Filtration Corp.
Inland Refining Co.
International Chemical Co.
International Coal Products Corp.
International Shoe Co.
Isabela Sugar Co., Phil. Is.

James Bradford Co.
Jas. Beach & Sons
J. B. Williams Co.
J. E. Rhoads & Sons
Jno. H. Heald & Co., Inc.
John W. Masury & Son
Jos. Schlitz Beverage Co.
J. S. McCormick Co.

Kauffman Lattimer Co.
Kewaunee Mfg. Co.
Keystone Fruit Products Co.
Kirkman & Son
Klearflax Linen Rug Co.
Kokomo Rubber Co.
Kolynos Co.

Laclede-Christy Clay Products Co.
Laclede Gas Light Co.
Lattimer-Goodwin Chemical Co.
L. D. Caulk Co.
Lever Bros. Co.
Lindsay Light Co.
Loose-Wiles Biscuit Co.
Los Angeles Soap Co.
L. R. Christie Co.
Lysander Kemp & Sons

McCormick & Co., Inc.
Magnetic Mfg. Co.
Manierre Engineering & Machinery Co.
Marley Paper Mfg. Co.
Mass. Cotton Mills
Mennen Co.
Metakloth Co.
Michigan Portland Cement Co.
Midland Linseed Products Co.
Minnesota Steel Co.
Mississippi Glass Co.
Mohawk Valley Cap Factory
Morris & Co.

National Biscuit Co.
National Fibre & Insulation Co.
National Filter Cloth & Weaving Co.
Naugatuck Chemical Co.
New Jersey Zinc Co.
Newport Chemical Works
Newton Falls Paper Co.
Norfolk Testing Laboratories
Northwestern Chemical Co.

Oakland Chemical Co.
O'Brien Varnish Co.
O. F. Zurn Co.
Ohio Brass Co.
Ohio Fuel Supply Co.
Ohio Grease Co.
Onondaga Pottery Co.
Orono Pulp & Paper Co.
Otis Steel Co.
Owens Bottle Co.

Pacific Coast Syrup Co.
Package Paper & Supply Corp.
Paper Makers Chemical Co.
Paraffine Cos., Inc.
Peerless Color Co.
Pennsylvania Salt Mfg. Co.
Pennsylvania Smelting Co.
Perkins Glue Co.
Pfeiffer Color Co.
Pfister & Vogel Leather Co.
Pillsbury Flour Mills Co.
Pittsburgh Plate Glass Co.
Pleasant Valley Wine Co.
Postum Cereal Co., Inc.
Potter Drug & Chemical Corp.
Prest-O-Lite Co., Inc.
Prince Mfg. Co.
P. W. Drackett & Sons Co.
Pure Food Factory "Hansa."
Pyrolectric Instrument Co.

Radium Co. of Colorado
Ralph L. Crosthwaite Co.
Refinite Co.
Republic Creosoting Co.
Roxana Petroleum Corp.

S. B. Penick & Co.
Sears, Roebuck & Co.
Seidlitz Varnish Co.
Seldner & Enequist, Inc.
Shepherd Chemical Co.
S. K. F. Industries
Solvay Process Co.
Southern Manganese Corp.
Southwestern Portland Cement Co.
Special Chemicals Co.
Spicer Mfg. Corp.
Spreckels "Savage" Tire Co.
Standard Oil Co. of Indiana
Standard Ultramarine Co.
Stauffer Chemical Co.
Sterling Products Co.
Stratford-Cookson Co.
Sun Co.
Swift & Co.
Swinehort Tire & Rubber Co.

Talc Products Co., Inc.
Thermoid Rubber Co.
Thomas Potter, Sons & Co., Inc.
Thompson & Co.
Trojan Powder Co.

Union Carbide and Carbon Research Laboratories, Inc.
Union Sugar Co.
Union Switch & Signal Co.
United Drug Co.
United Natural Gas Co.
United States Glue Co.
Upco Co.
Utah Oil Refining Co.

Vacuum Oil Co
Vesta Battery Corp.
Victor Talking Machine Co.
Virginia Smelting Co.

Warner-Jenkinson Co.
Warner Sugar Refining Co.
Weirton Steel Co.
Welsbach Co.
Western Reserve Rubber Co.
Western Sugar Refinery
West Virginia Pulp & Paper Co.
W. H. Daugherty Refining Co.
Wilbur White Chemical Co.
Wilson & Co.
W. P. Tanner-Gross & Co., Inc.
Wm. Wrigley Jr., Co.

York Chemical Works

The ordinary citizen probably does not realize the fact that his scales, of no matter what size, can be supplied with one or two extra parts at a slight expense which would convert them to the metric system.

Another firm remarks, "When once the advantages of the metric system are realized, the public will wonder why it was not forcibly adopted long ago."

Cream separators and steam turbines are being made on metric specifications. Here is *another* product although the letter does not disclose the nature of the product. It states, "We shall be glad to coöperate. We have used the metric system exclusively in our manufacturing for thirty years. It would be great if we could buy and sell in the same language in which we manufacture."

A chemical company writes, "We have been in the habit of specifying quantities in the metric system on our orders for the laboratory chemicals."

A refiner of sulfur packs and sells his product in metric units:

> We have for some time been packing our sulfur in 50-kilo sacks to conform with the metric standard of weights and measures. We have also been endeavoring to pack our barrels also according to metric weights, but as the trade is accustomed to certain sized barrels we have not as yet been able to accomplish this, but expect within a short time to have all of our packages conform with the metric system which we consider much more satisfactory than the old system of weights.

Several correspondents desire to go *further* than the committee has requested:

> We shall be very pleased to coöperate with the Metric System Committee by placing all of our orders for chemicals and chemical apparatus in the metric system, so far as it will be possible to obtain service in this way.
>
> We should, if possible, like to go even further than this and purchase our chemical raw materials in the metric system, but we fear that this may not be possible.

Another writes, "We shall do all in our power to encourage the use of the metric system among commercial heavy chemicals."

And another states:

> You can rest assured that this company will do what they can to coöperate in this matter and will be glad to specify our requirements in the metric system when we feel reasonably sure that they can be interpreted correctly by the company from whom we are purchasing material. As a matter of fact we feel reasonably certain that the majority of our raw materials are purchased from companies who will be glad to coöperate in this movement.

Others urge the committee to strive toward legislation, because so long as customs and freight rates are adjusted on English weights our progress is limited.

> This firm heartily indorses the movement to introduce the metric system. At various occasions we placed before our state representatives at Washington the importance of adopting the metric system of weights and measures. Upon being questioned as to the advisability of using the metric system in our business, our stand has always been very favorable.
>
> We firmly believe it to be a step in the right direction to order laboratory supplies and chemicals in the metric units as far as practical.

A large oil company states:

> It has been our habit wherever practicable for several years past to place our orders in this way for laboratory supplies. In future we shall very gladly order all materials, both chemicals and apparatus, in metric units, as recommended by your committee.
>
> Beside fine chemicals, we of course use large quantities of heavy chemicals in the refining of petroleum. At present it is manifestly impracticable to purchase these in metric units. When, however, you have succeeded in lining up the country's industries under your banner, you will not find us in the rear.

One company manufacturing chemical apparatus sees a difficulty:

> We are willing to give our support to the metric system as far as possible, but would state that we believe our principal difficulty will be with the workmen who have to use the chemicals in fulfilling the practical process work. They do not know the least thing about the metric system.

This difficulty, however, is being solved by the chief chemist in a glass works:

> We are in sympathy with the movement to aid in the transition to metric units, and although our purchases of chemicals (laboratory) are small, I shall be glad to order them by metric weight and measure.
>
> I am planning to give a lecture on the metric system for our machinists, mold-makers, and others in the plant, in connection with Industrial Y. M. C. A. work.
>
> In the purchasing of heavy chemicals for glass making, I feel that it will be impractical to depart from the English ton and pound basis, until the R. R. freights are reckoned on a metric basis.
>
> Among our shipping crew, a certain degree of familiarity with kilos is developed by handling export packages. Some other measurements, such as caps for jelly glasses, are also metric.

England is holding us back according to another manufacturer, "As an officer of a concern manufacturing rare chemicals and shipping same abroad, especially to England, in considerable quantities, the introduction of this system is not very practical at the present time."

But we must not hold England back, and then, too, conditions in England may change just as they are changed in Japan and Poland.

Quite unsolicited, comes the following: "The Hampton Roads Chemists' Club most heartily indorses the program of the Metric System Committee and faithfully pledges to support the movement by ordering chemical supplies by metric weights and measurements." We recommend this action to our local sections.

Several purchasers have been misled by the rough conversion table published by J. T. Baker into supposing that the users of metric weights are being penalized. We can state on the authority of Mr. Baker himself that this is not intended and customers should observe that they secure full weight. Since 1 kg. = 2.205 lbs., "500 grams 10 per cent above 1 lb., 1 kg. 2.2 times 1 lb." is sufficiently correct for an approximation.

We are able to extend our list of those manufacturers and dealers who are able to quote supplies on a metric basis (Table II). To anyone desiring them, "stickers" will be sent to be affixed to all lists sent to manufacturers and dealers.

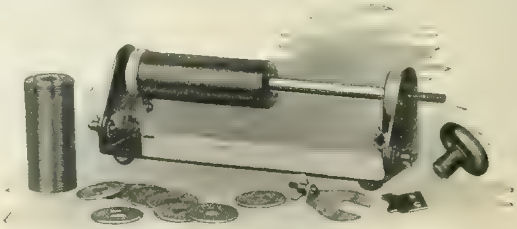
TABLE II—SUPPLEMENTARY LIST OF MANUFACTURERS AND DEALERS WHO ARE PREPARED TO SUPPLY GOODS ON METRIC SPECIFICATIONS

American Pharmaceutical Co.
Arthur H. Thomas Co.
Aspirin Company of America
Central Scientific Co.
Edward P. Dolbey & Co.
E. H. Sargent & Co.
Leonard Danziger
Newark Wire Cloth Co.
Powers-Weightman-Rosengarten Co.
Pyrolectric Instrument Co.
William Gaertner & Co.

A Laboratory Rheostat

The Allen-Bradley Co., manufacturers of electric controlling apparatus at Milwaukee, Wis., has placed on the market a rheostat which is well adapted for current control for electric combustion and muffle furnaces, and for general laboratory use where portability and flexibility are of importance.

The rheostat is of the graphite compression type. As shown in the accompanying cut, it consists of a column of treated graphite disks mounted on an insulated rod. It has a normal capacity of 200 watts, but will stand 500 to 1000 watts under momentary loads. It will carry a maximum of 40 amperes continuously, and can be used on either direct or alternating current circuits up to 250 volts.



The resistance of the rheostat is dependent on the treatment of the disks. It is possible to assemble rheostats with a minimum resistance of 0.01 ohm, or they may be made of disks which will give 30 ohms or more under pressure. Since when all pressure is released from the column the resistance is approximately one hundred times as great as when the disks are under full compression, the maximum resistance in these two rheostats is 1 and 3000 ohms, respectively.

Recent Advances in Plant Chemistry[1]

[ABSTRACT]

By R. W. Thatcher[2]

New York State Agricultural Experiment Station, Geneva, New York

THE study of the chemistry of plant life is one of the most recent phases of the development of the science of chemistry. Economic interests have always stimulated metallurgical research and studies in connection with processes of industrial manufacture of organic compounds. Interest in public health problems has been a powerful stimulus to the study of the chemistry of physiological and pathological processes of animal life. But similar studies of the chemistry of plant life have been, for the most part, left to the botanists or to an occasional biochemist who has had as his impelling motive a keen interest in the works of Nature as manifested in the growth of plants. Even so-called "agricultural chemists" have devoted most of their energies to the problems of supplying anergic foods to plants in the form of fertilizers, or to the problems of animal nutrition, or to the inspection service in connection with the regulation of the sale of agricultural products to or from their ultimate consumer.

Recently, however, there has appeared in the plans and the writings of a few biochemists the idea that the study of the synthetic activities of plants offers a fascinating and fruitful field both for scientific inquiry and for economic development.

Undoubtedly the most serious handicap which biochemists have had in their attempts to study or duplicate the chemical processes which take place in cell protoplasm lies in the fact that they have thus far been compelled to work with mixtures of reagents in solution, contained in beakers, test tubes, etc., in which ionization and diffusion make a uniform chemical change throughout the entire reacting mass practically unavoidable. Recent advances in our knowledge of the colloidal condition make it plain, however, that even in so small a mass as the protoplasmic contents of a single cell there are thousands, if not millions, of colloidal compartments, separated from each other by membranes of variable and perhaps constantly varying permeability, in which a great variety of chemical changes may go on independently of each other.

It seems to me, therefore, that the first requisite for up-to-date study of the chemistry of living things is a recognition of the *structure* of the cell as an essential factor in its synthetic operations, and that the first advancement toward an understanding of and possible duplication of the cell synthesis will require the successful reproduction of a colloidal mass having similar structure to that of cell protoplasm.

A proper mental picture of the organization and activity of a plant cell is suggested by the figure of a well-organized chemical factory, with the different transformations which are involved in the whole process going on in different parts or rooms of the factory, with the raw materials systematically transported from one room to another as they are needed to keep each step in the whole process going at the proper rate; and with all the different parts of the whole factory working in smooth coördination with each other.

The raw materials for this factory are the mineral matter and water coming from the soil and the gases of the atmosphere; the intermediates are the simple carbohydrates and amino acids; and the finished products comprise all of the varied compounds which are the results of cell protoplasmic activity and which are used by the plant for its nutrition, growth, or reproduction.

The researches of botanists and chemists in the past have dealt with the nature of the compounds and the chemical changes which are involved in each separate process of the factory's operation. The principal problem now is to learn the nature and method of superintendence of the factory, whereby its operations are automatically regulated and altered so as to provide the proper output of all the varying products of the factory to meet the needs of the whole plant. We are as yet almost wholly in the dark concerning the regulatory agencies which control the rate and character of the synthetic processes of cell operation. We call these regulatory agents catalysts, or enzymes, but as to what they are and how they act we know very little.

Furthermore, we have absolutely no idea of the methods of intercommunication and of recognition of supplies and needs of raw materials or finished products whereby the factory output is varied in kind or quantity to meet the needs of the growing plant. We say, more or less empirically, that "hormones" stimulate certain cell activities. But what are hormones, and how do they happen to be in the right place and at the right time to start the factory operation as it is needed? We speak glibly of "inhibitors" which slow up or stop any given process when its products accumulate in quantities unsuitable for the proper functioning of the plant organism; but we know little of their nature or origin.

In my opinion, therefore, the most significant contributions to our knowledge of the chemistry of plant life in recent years are those which deal with the phenomena associated with the colloidal conditions of matter and with the catalysts, stimulants, and inhibitors which serve to regulate both the direction and the velocity of the chemical reactions which, taken as a whole, constitute the vital phenomena.

I regard as one of the most promising fields of investigation of plant chemistry the apparently simple, but as yet little understood, relation of water to the colloidal condition of organic materials. The recent preparation of an artificial gel which is so nearly solid that it can be cut into blocks with a knife and from which no water can be squeezed out, which yet contains less than 0.3 per cent of solid matter, is an illuminating example of the possibilities of almost infinite dispersion and of the extent to which surface boundary phenomena may be brought into play in semisolid colloidal masses like that of plant protoplasm. The constant changes in concentration of dissolved solids by colloidal imbibition of water, and the protection of protoplasm against injury by extreme changes of temperature, as well as the adaptation of plant protoplasm to its environmental surroundings are all definite chemical phenomena which may well find their explanation in the water relations of the colloidal mass.

A further aspect of plant chemistry, the significance of which is easily apparent from the simile of the factory, is that chemical changes which are almost the exact antithesis of each other are going on simultaneously in every active plant organism, if not indeed in each individual plant cell. The synthetic production of complex organic compounds and the destructive oxidation of previously produced synergic foods to furnish energy for the synthetic processes go on simultaneously; just as, in any factory, there is consumption of fuel, wearing out of equipment, etc., during the process of manufacture of the factory output. This phenomenon, too, is readily understood on the basis of colloidal structure and emphasizes again the importance of recognition of this condition of matter as a necessary step in studies of protoplasmic activities.

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[1] Presented before the Rochester Section of the American Chemical Society, Geneva, N. Y., October 1, 1921.

[2] Director of Experiment Station.

Pyrex: A Triumph for Chemical Research in Industry[1]

By W. H. Curtiss

Corning Glass Works, Corning, New York

WHAT does the word "glass" mean to the ordinary man? He thinks of a hard, transparent substance easily broken. These two properties, transparency and breakableness, are universally connected with glass in the public mind. To be sure, not all glass is transparent; but transparency governs the most familiar uses of glass and it may be regarded as its most important property. Ease of breakage, on the other hand, is and always has been a basic handicap in glass, and has profoundly influenced the character of its uses. So inseparable from glass has this quality been regarded that until recently glass manufacturers gave no serious thought to the possibility of modifying the extent to which glass, under various conditions, is breakable.

The first deliberate study and efforts by a manufacturer of glass in the United States to produce a glass of superior mechanical strength and with real qualities of heat and chemical resistance were made by Corning Glass Works of Corning, New York. The Corning Glass Works had the specific problem to solve of devising a glass for the inner globe of street arc lamps that would resist the intense heat generated by the arc and the extreme temperature variations incident to outdoor use, and its efforts were at first instigated by this problem. There was little to guide them in their study. The pioneer work of Otto Schott of Jena had shown that of the six factors or properties determining the ability of glass to withstand sudden changes in temperature the linear expansion coefficient could be most easily and widely varied. Disregarding quartz glass and speaking only of glasses that can be melted and worked by usual methods, the expansion of glass can be varied in the ratio of six or more to one. The other properties influencing heat resistance cannot be varied over any such range. Corning's line of research, therefore, was toward a glass of low linear expansion; but in securing that property the composition could not be varied in directions that would adversely affect the melting and working qualities of the glass.

Glasses having expansion as high as 0.000014 have been made without difficulty. Ordinary lead glass has an expansion of 0.0000092, while lime glass has a somewhat higher coefficient. When Corning Glass Works commenced its experiments, a Jena glass was known having an expansion coefficient of 0.0000064. This was the Jena thermometer glass 59''' and was a borosilicate glass. Here then was one indication that assisted the early experiments—the glass known at the time that had the lowest coefficient of linear expansion was a borosilicate glass.

The Jena 59''' glass and other glasses having somewhat similar properties were tested and analyzed; and glasses duplicating these properties were manufactured on a small scale. At first the commercial application was limited to inner arc globes and battery jars; but later the glass was applied also to railroad lantern globes, the need having long been felt for a heat resisting glass to meet the severe service exacted of such globes. These early glasses of Corning were successful to an extent that justified the Company in establishing the first properly organized research laboratory in the glass industry in the United States.

The laboratory organization carried on in a more intensive fashion the work already started in modifying the known borosilicate glasses in the direction of lowering their expansion. One of the chief difficulties experienced was the maintenance of stability in the glass as the expansion was lowered. Efforts were concentrated on this problem with the result that a glass was soon developed combining low expansion with sufficient stability so that it became the standard for lantern globes, chimneys, inner arcs, and battery jars, practically eliminating from the market ordinary glass previously used for these products. To this glass the trade-mark Nonex was applied. The application of the glass to railroad lantern globes demanded a separate line of research to develop suitable colors for standard railroad signal work. Much of this research was in distinctly new channels, because the usual materials for producing red, green, blue, and yellow hues had a radically different effect when introduced into the new heat resistant composition. It is sufficient to say that this problem was completely solved and that all the standard railroad colors are regularly produced in Corning low expansion glasses.

The steady progress made by Corning Glass Works' laboratory toward the definite goal that had been set from the beginning of their research, and the great commercial success attained with the heat resisting glass products that had been marketed, paved the way for what was perhaps the most daring and most distinctly novel idea for an application of heat resistant glass that had yet been made—the use of it as a material for oven cooking utensils. To attain any measure of success in this field it was necessary to intensify and increase all of the effects already secured in the new glass. The heat resistant quality must be improved, for a thick walled baking dish subjected to oven heat represented a severer test than any service required of lantern globes or chimneys; it must have still greater resistance to the corrosive action of liquids; and it must be strong enough mechanically to stand the rough usage of the ordinary kitchen. The first large shipment of baking ware, now known throughout the world as Pyrex, was made by Corning Glass Works in May 1915, after several years of intensive study and experiment and after wide distribution of such ware made for test purposes.

During the year 1914, a new commercial application for this versatile glass, of vital significance to the chemical industry, was undertaken in a small way. In that year flasks, beakers, and laboratory apparatus were first made. As has been pointed out, development of a successful oven cooking glass had necessitated great improvement in heat resistance and nonsolubility. These very qualities gave, ready to hand, a laboratory glass superior to any known glass, foreign or domestic. American laboratories, both industrial and educational, had long depended for their glass apparatus on the foreign makers. Jena glasses had been regarded as the standard of the world in this field; but when the war caused the gradual drying up of imports from Germany, Corning was fully prepared to help the American chemist in his difficulty. Chemists throughout the country, knowing of the remarkable properties of Pyrex from its other demonstrated uses, virtually demanded it for their laboratories; and the Government itself seconded this demand when war industry and research enormously increased the use by the Government of chemical glassware. It was in the spring of 1915 that Corning placed on the market a complete line of flasks, beakers, test tubes and fabricated apparatus in Pyrex—a line that has grown steadily in popularity till now scarcely a laboratory in the country is without its quota of Pyrex chemical ware. Foreign chemists, too, have recognized the value of Pyrex, which is now invading the home markets of the best foreign glass in steadily increasing quantities.

Pyrex should not be regarded as a *substitute* for the glasses of Jena and other foreign laboratory-ware makers. By test and

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[1] Received February 28, 1922.

by the expression of thousands of chemists it is distinctly superior to these glasses, and has supplanted them on its own merits. The United States Bureau of Standards[2] gives to Pyrex a higher rating than to any other known glass. Details of the tests by which this rating was determined need not be repeated here except to say that the linear expansion of Pyrex was found to be 0.00000334, of the best foreign glass 0.00000479; while the solubility of Pyrex in water was less than half that of the foreign product.

To dismiss in these few paragraphs the intensive development and research preceding the year 1915 gives an entirely inadequate picture. Aside from continued progress along the main research path—the lowering of expansion and improving of stability in the glass itself—there were other major problems arising from its radically different melting and working conditions. It was decidedly more refractory than ordinary glasses, requiring an exceptionally high temperature for melting. The highest skill in the art of glass melting was required to perfect the commercial production of Pyrex on a large scale. This same refractory quality meant that the glass "set" more rapidly than softer glasses, and quicker methods of working and handling had to be devised.

Mention should here be made of the discovery of a very important property of glass in its use as baking ware. It bakes food more rapidly and thoroughly than ordinary utensils of metal. This was found to be due to the greater reflectivity of the metal for radiant energy. It has been determined that silver reflects about 90 per cent of radiant heat rays, while glass reflects only about 14 per cent. Ordinary utensil metals would be lower in reflectivity than silver, but still comparable to it and very much higher than glass. A series of experiments demonstrated the practical importance of this property of glass as a baking utensil and its superiority to any other oven utensil in commercial use.

It should be borne in mind that research work for improving Pyrex and for widening its commercial uses is by no means finished; in fact, the present applications of Pyrex, diverse as the appended list shows them to be, are believed to represent only a beginning of the possibilities in this remarkable glass; and Corning's laboratory organization is making constant progress in perfecting new uses for it. Of particular interest to the chemical industry will be the logical step from the laboratory use of Pyrex to actual production uses in chemical manufacturing plants. It is confidently expected that Pyrex products will soon replace more expensive and less reliable materials in chemical plants for conveying liquids at high temperatures, for volatilization and for kindred uses.

The scope of the present article will not permit of a detailed treatment of the many other eminently successful lines of research by the laboratory of Corning Glass Works. The development of Pyrex is only a typical example of the contributions of that organization to glass chemistry. Brief mention may be made, however, of the most important of those contributions which have placed America in a leading position in the manufacture of glass for various practical, industrial, and scientific uses. Potash glass was formerly considered essential for incandescent electric light bulbs. The war, by shutting off imports of German potash, made action imperative in the direction of a substitute glass. First, a successful non-potash lead glass was produced, and later a lime glass, which has largely replaced all other glasses in the making of incandescent bulbs in this country. Colored glasses of various special properties have been developed, embracing the high transmission railroad signal colors; a glass absolutely duplicating daylight; glasses absorbing certain definite portions of the spectrum, such as the ultraviolet or the infra-red rays; X-ray shield glasses; spectacle glasses for work in special conditions of heat and light. Each of these deserves a chapter in the story of chemical research in industry, but must here be dismissed with only this mention.

PRESENT PRODUCTS OF PYREX

Oven cooking utensils
Oven door panels
Percolator tops
Coffee urn liners
Gage glasses
Cylinders
Tubing
Flasks, beakers, test tubes
Fabricated laboratory apparatus
Battery jars
Lantern globes
Chimneys
Condenser lenses
Headlight glasses

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[2] Walker and Smither, "Comparative Tests of Chemical Glassware," *Bur. Standards, Tech. Paper* **107** (April 5, 1918).

Corrosion

The National Research Council recently appointed a committee with its Division of Research Extension with the following membership:

W. M. Corse (*Chairman*), General Manager, Monel Metal Products Corporation, Bayonne, N. J.
John Johnston, Yale University, New Haven, Conn.
D. M. Buck, American Tin Sheet and Tin Plate Co., Frick Building, Pittsburgh, Pa.
Colin G. Fink (*Secretary*), 101 Park Ave., New York, N. Y.
Wilder D. Bancroft, Cornell University, Ithaca, N. Y.
G. K. Burgess, Bureau of Standards, Washington, D. C.
William H. Bassett, American Brass Co., Waterbury, Conn.
E. M. Chamot, Cornell University, Ithaca, N. Y.

The purpose of this committee is to serve as a general clearinghouse and to devote its attention essentially to fundamental scientific study of corrosion. This committee desires to get in touch with all the work that is being done on corrosion whether through societies, associations, institutions, universities, or private or industrial laboratories. It is known that the following committees are at work, or have been recently appointed to undertake work:

American Society for Testing Materials—This Society has had a committee on corrosion of iron and steel for a number of years known as Committee A-5. Mr. J. H. Gibboney, chemist of the Norfolk and Western Railroad, Roanoke, Va., was designated as acting chairman of the committee, following the death of Dr. S. S. Vorhees of the Bureau of Standards, and the secretary is Mr. J. A. Aupperle, chief chemist of the American Rolling Mill Co., Middletown, Ohio. The committee is representative of both nonproducers and producers of iron and steel with four subcommittees, one an advisory committee, another a committee on preserving metallic coatings of metals, another a committee on inspection, and the last a committee on total immersion tests. It has been decided to establish a further committee (Committee B-3) on corrosion of nonferrous metals and alloys, representing nonproducers and producers.

The American Committee on Electrolysis was organized in 1913 through the activity of some members of the American Institute of Electrical Engineers, representing, in addition to the Institute and the Bureau of Standards, the following organizations:

American Electric Railway Association, American Gas Association, American Railway Engineering Association, American Telephone and Telegraph Co., American Water Works Association, National Electric Light Association, National Gas Association of America. This committee is made up of twenty-seven engineers, three from each of the organizations named. This general committee appointed a special research subcommittee of which Mr. H. S. Warren, 195 Broadway, New York City, is chairman, and Mr. H. C. Sutton, 1401 Arch St., Philadelphia, Pa., is secretary. The Bureau of Standards undertook the investigation of certain phases of the electrolysis problem in 1910 and has since then made important contributions to the subject. At the beginning of the coöperative work between the Bureau and the Research Subcommittee a policy was agreed upon to the effect that the investigations are solely concerned with the accumulation of facts leading to the establishment of principles upon which conclusions and recommendations may ultimately be based. Mr. Burton McCollum, of the Bureau, has recently proposed an extended series of tests of samples of many kinds of pipe buried in the soils of known special character in selected localities in many parts of our country.

Engineering Foundation is giving preliminary consideration to a study of that form of corrosion of iron which has been called "Graphitic Corrosion."

The American Electrochemical Society at its recent meeting named Dr. Colin G. Fink as head of the committee on corrosion investigations.

The Bureau of Mines at its Pittsburgh Station is investigating the corrosion of mine waters on metals.

The American Society of Civil Engineers has recently appointed a research committee of which Prof. A. M. Talbot at the University of Illinois, Urbana, Ill., is chairman, and F. E. Schmitt, Associate Editor, *Engineering News Record*, 10th Ave. and 36th St., New York City, is secretary. The matter of corrosion has not yet been considered by the committee, but undoubtedly will be.

Some associations, like the National Canners' Association, and certain corporations like the New Jersey Zinc Company and National Tube Company, have been making studies in corrosion. The committee of the National Research Council will be very glad to be informed of any work on corrosion that is going on or that is in contemplation. Communications should be sent to Paul Moore, Secretary, Division of Research Extension, National Research Council, 1701 Massachusetts Ave., Washington, D. C.

Problems in Corrosion

By Colin G. Fink

SECRETARY, CORROSION COMMITTEE, NATIONAL RESEARCH COUNCIL

In spite of the general relaxation in chemical and metallurgical research throughout the country, a number of the corrosion problems are so very important and their solution involves such large savings in capital and labor, that a number of concerns and government laboratories felt the urgent need of furthering corrosion research during the last year.

The corrosion problems have been attacked from two more or less different angles. In the one case every effort is being made to arrest the corrosion of the materials now in use; in the second case, new materials are substituted and tried out. There are to-day a series of distinct corrosion problems, in each instance centered about some specific material or article of manufacture. There is, for example, the problem of the corrosion of food containers and the problem of the corrosion of buried conduits and cables. Besides these specific problems, there are the general investigations on the causes of corrosion under varying conditions and of various materials.

We cite below a few of the corrosion problems covering specific materials or products; and, secondly, a few of the general topics, closely allied to the corrosion problem, which require further study and research.

CORROSION PROBLEMS ARRANGED ACCORDING TO SPECIFIC MATERIAL

Condenser tubes
Underground cables
Buried iron pipes, posts, etc.
Fence wire
Flues, stacks, stove pipes
Steel ships and ship fittings
Roofing materials
Mine pumps and other mine equipment
Atmospheric corrosion of brass
Atmospheric corrosion of bronzes
Alloys resistant to high temperatures
Corrosion of zinc cathodes
Contact metals or alloys
Catalyzer metals or alloys
Cutlery steels
Acid tank linings
Corrosion of nickel plated ware
Boiler tubes
Fire boxes
Automobile radiators
Insoluble anode
Corrosion of iron as affected by presence of small amounts of other elements

GENERAL PROBLEMS

Velocity of corrosion as affected by:

(*a*) Temperature fluctuations.
(*b*) Alternate dry and moist surface.
(*c*) Presence of foreign materials.
(*d*) Presence of oxide, carbonate or other compound of one or the other constituent of the alloy.
(*e*) Crystal structure and intercrystalline cement.

Properties of the surface film:

(*a*) Coefficient of expansion as compared with that of the underlying metal.
(*b*) Chemical composition.
(*c*) Porosity.
(*d*) Flexibility or ductility.
(*e*) Coefficient of adhesion.
(*f*) Speed of renewal or "healing."
(*g*) Relative hardness.
(*h*) How affected during mechanical working.

Corrosion and bacteria.

A more complete micrographic investigation of the changes taking place in the film and the metal underneath, during the process of corrosion, is very desirable. Furthermore, we shall be able to progress more rapidly the sooner we agree upon standard tests used to determine the relative corrodibility of two samples. At present it is almost impossible to compare the results of one author with those of another, even when both have used the same materials in their tests.

Within the last year decided progress has been made in cutlery steels, in metals and alloys for mine equipment, in cable sheath, in insoluble anodes and in alloys resistant to high temperatures and the corrosive action of molten metals such as zinc, tin, etc. But the corrosion problem, as a whole, in spite of its long past history, is still in its "infancy" and it is only through coöperative effort and a free discussion of results (those suitable for advertising purposes as well as those usually suppressed) that consistent forward strides are possible.

Chemistry by Radio

The interest taken by nearly a million people in wireless telephony and the programs prepared for broadcasting from various centers affords an opportunity which is being utilized by chemists. The Publicity Committee of the Detroit Section, under the leadership of H. C. Hamilton, is to have five minutes each week on the program prepared by the Detroit *News*. The first of these was given on March 16, "Chemistry as We Meet It Every Day" being the subject.

On the 18th from the Westinghouse Station in Pittsburgh the Pittsburgh Section, through the Chairman, J. O. Handy, arranged for ten minutes which was devoted to a popular story on "Chemistry in Peace and War," by H. E. Howe.

In many other localities chemists can do service to the profession by telling over the wireless telephone the fundamental place which chemistry occupies in everyday life and in all the industries.

NOTES AND CORRESPONDENCE

Visit to Local Sections

The Editor and the Technical Manager of the A. C. S. News Service spent the greater part of March visiting the local sections in the Middle West. The trip was made to learn through personal contact with the members just how the JOURNAL can be made more useful to the chemical industry and the chemical profession. Mr. Garnett accompanied the Editor in order that he might confer with the local sections with a view to mapping out some policy to be followed in obtaining local publicity and to explain personally to the sections visited that the News Service is at their service at any and all times, and that in order to make it a success they must make the greatest possible use of it.

In all, seventeen sections were visited, including

Eastern New York
Syracuse
Western New York
Northern Indiana
Cleveland
Detroit
University of Michigan
Midland
Michigan Agricultural College
Chicago
Indiana
Lafayette
Louisville
Lexington
Cincinnati
Columbus
Pittsburgh

Mr. Garnett joined the Editor at Buffalo and accompanied him on the remainder of the trip, except that they separated on two occasions in order to cover more ground, the Editor going to South Bend and Lafayette, and Mr. Garnett to Cleveland and Louisville. At each place they were entertained by the section and discussed the JOURNAL and News Service with the entire section or members of the Executive and Publicity Committees.

About 200 were present at the intersectional meeting at Northwestern University on March 11, at which the Milwaukee, Wisconsin, Iowa, and Illinois sections were represented. Professor J. H. Mathews presided at the afternoon meeting, and considerable discussion, in which eight or ten participated, followed the Editor's address. At the evening meeting, over which Dr. W. Lee Lewis presided, the following greetings were given: For the SOCIETY, H. E. Howe; Illinois, A. M. Buswell; Wisconsin, H. B. Adkins; Milwaukee, E. J. Kern; Iowa, Edward Bartow. A paper by G. L. Wendt on "The Atomic Disintegration of Tungsten" was read, and a congratulatory resolution was passed and sent to the author.

On the afternoon of March 11 they were guests at luncheon of the Chicago Chemists' Club, where they met present and past editors of the *Chicago Bulletin* and the editorial staff.

At Indianapolis the Editor also addressed the Scientech Club on "The Universality of Chemistry."

It is believed that a better understanding by both the stockholders and the members of the JOURNAL staff resulted from the trip which will be to their mutual advantage and will go a long way toward solving the problem of getting chemistry across. The results of the trip were so gratifying that similar trips in other directions are on the calendar for a later date.

New Local Sections, A. C. S.

A Section of the SOCIETY, known as the Purdue Section, was organized January 10, 1922, with a membership of 50 active and 14 associate members. Its officers are:

Chairman: L. A. TEST
Secretary-Treasurer: MARGUERITE G. MALLON
Vice Chairman: A. J. WILSON
Councilor: E. G. MAHIN

The Northern Indiana Section, with headquarters at South Bend, numbers 54 members. The following officers were elected at its first meeting, January 19:

Chairman: M. M. MACLEAN
Secretary: V. C. BIDLACK
Vice Chairman: E. N. WEBER
Treasurer: S. J. MCGRATH
Councilor: H. B. FRONING

Officers of the Institute of Metals

At the annual meeting of the American Institute of Mining and Metallurgical Engineers held in New York the week of February 20, 1922, the following were elected officers of the Institute of Metals Division:

Chairman: W. B. PRICE, Scovill Mfg. Co., Waterbury, Conn.
Vice Chairman: GEORGE K. ELLIOTT, Lunkenheimer Co., Cincinnati, Ohio.
Secretary-Treasurer: W. M. CORSE, Monel Metal Products Corporation, Bayonne, N. J.
Executive Committee:
GEORGE K. ELLIOTT.
C. T. BRAGG, Michigan Melting and Refining Co., Detroit, Mich.
H. M. LANE, H. M. Lane Engineering Co., Detroit, Mich.
LAWRENCE ADDICKS, New York, N. Y.
WILLIAM CAMPBELL, Columbia University, New York, N. Y.
J. A. CAPP, General Electric Co., Schenectady, N. Y.
E. E. THUM, McGraw-Hill Book Co., Inc., New York, N. Y.
GEORGE F. COMSTOCK, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.
W. A. COWAN, National Lead Co., Brooklyn, N. Y.
H. M. WILLIAMS, c/o General Motors Research Corporation, Dayton, Ohio.

Employment for Chemists

Editor of the Journal of Industrial and Engineering Chemistry:

"Our Unemployment Problem," as described in your editorial in the February 1922 issue of THIS JOURNAL, brought very forcibly to my mind a letter addressed to me, long ago, by Professor Henry Wuyts of the University of Brussels, giving his opinion that the future logical center of chemical development, scientific as well as industrial, is bound to be in the United States, and I am absolutely of the same opinion.

There is room in all our large industries, right now, for many more able, willing, intelligent, and industrious chemists than are available, and I have no doubt that such deserving chemists will soon be placed.

Many industries appreciate the invaluable help of their research departments, and consider them their most potential element of earnings. The richest men like Carnegie do not hesitate to give chemistry full credit for their success. We have many excellent chemists in the United States who have produced wonders, a very great number who have efficiently helped their concerns, unluckily, too great a number have proved to be only a burden, and let us hope, only a few have brought disrepute on their profession, but I have heard it said, by more than one manufacturer, that some chemists have misused information obtained in their employ and this has caused distrust. Undoubtedly the profession, like all others, needs some well-defined standards of ethics and perhaps an enforcement organization as other professions have.

Chemistry is not fully appreciated by the layman, but even he is rapidly learning to value scientific research.

There is no doubt that every chemist worthy of the name and of his great profession will find an enviable place, as conditions are undoubtedly rapidly improving in all industries.

PAUL SEYDEL

THE SEYDEL MFG. CO.
JERSEY CITY, N. J.
February 17, 1922

The Determination of Glycerol in the Presence of Sugars—Correction

In the article of the above title, published in THIS JOURNAL, 14 (1922), 54, there is an error which requires correction.

Equation 4 on page 56 should read $D = \frac{C \times 0.01 \times 20 \times 100}{1.25} = 16\ C.$

LARKIN CO., INC.
BUFFALO, N. Y.
February 7, 1922

L. F. HOYT
H. V. PEMBERTON

Calendar of Meetings

American Electrochemical Society—Spring Meeting, Baltimore, Md., April 27 to 29, 1922.

American Institute of Chemical Engineers—14th Semiannual Meeting, Niagara Falls, Ontario, June 19 to 22, 1922.

American Society for Testing Materials—25th Annual Meeting, Atlantic City, N. J., June 26 to July 1, 1922.

WASHINGTON NOTES

THE DYE PROBE

Chemically speaking, the interest of the month has been focused in and around the Capitol. On February 20 the committee appointed to investigate the alleged dye probe was reorganized. Senator Shortridge continued as chairman, with Senators Ashurst of Arizona and Sterling of South Dakota as the other members, Senators Ernst and Reed having previously declined to serve. Senator Ashurst has since resigned from the committee and no one has been designated to fill the vacancy thus created. The hearings have been conducted almost continuously since they started and give promise that they will drag on for many weeks to come. The representatives of the domestic dye industries are very much pleased with the course of the investigation, which has given them exactly the opportunity they wanted to prove to the committee and to the country at large that there is not and never has been a monopoly among domestic dye manufacturers and that they have not attempted to influence Congress improperly. No one in attendance at the hearings could fail to be impressed by the straightforward testimony, made under oath, of these men who have been putting up such a long, hard fight to protect the American dye industry. Their cards are all on the table and they not only welcome but invite the closest study and scrutiny of the evidence submitted. Their attitude is best expressed by Francis P. Garvan, President of the Chemical Foundation, when he said:

> As long as this committee may sit it cannot find a witness to give one iota of evidence which would stand in any court of justice as tending to show the existence of a monopoly in the American dye industry.

Contrast with that statement the attitude and statements of those hostile to the development of the American industry.

MUSCLE SHOALS

Muscle Shoals is still with us. The House Military Affairs Committee has considered the propositions of Ford, Engstrum, and the Alabama Power Company, and as we go to press is seeking the advice and opinion of experts who have no connection or personal interest in any of the proposals thus far presented to the committee for consideration. The committee has a great mass of evidence before it, and as it will take considerable time to analyze this evidence the final report cannot be looked for until some time after the hearings are concluded. The Senate Committee on Agriculture and Forestry on February 24 was authorized to take a trip to Muscle Shoals for the purpose of personally investigating the situation. Other members of the Senate requested permission to accompany the committee, with the result that about forty-five senators will compose the investigating party. Since the treaties are of all-absorbing interest in the Senate just now, however, it is probable that no action looking towards Muscle Shoals will be taken by that body in the immediate future.

PATENT CONVENTION WITH GERMANY

On February 17, the President asked the advice and consent of the Senate, in advance, to the revival of the convention of 1909 between the United States and Germany bearing upon patents. On February 22 the Senate passed a resolution advising and consenting to the giving of notice by the President to revive this convention. The President, however, has not notified Germany that the treaty is revived, which is all that is necessary to make the treaty effective, but on the contrary is withholding formal notification until important phases of patent legislation can be given careful consideration.

MORE SHORTSIGHTEDNESS

Congress has eliminated the appropriation of $35,000 for nonmetallics which was granted to the Bureau of Mines last year. This means that a large part of the work in nonmetallics will be discontinued. The money appropriated last year was greatly needed by the Bureau of Mines in the expansion of its nonmetallic work and the cutting off of it this year is a keen disappointment to the various industries affected, which number among them the heavy clay industry, talc, gypsum, feldspar, and similar industries, as well as to the Bureau of Mines officials.

HELIUM PRODUCTION

The lamentable disaster to the Roma has aroused keen interest in the question of the utilization of helium in place of hydrogen. It is generally recognized that if the Roma had been filled with helium instead of hydrogen the result would have been very different, and even though the ship were wrecked it is possible that no lives would have been lost.

The Army and Navy at the present time have on hand about 2,400,000 cubic feet of helium, but it was not used in the Roma for the reason that she was not especially adapted for its use and also because some of her bags were in a rather leaky condition on account of old age. The disaster has awakened interest in Congress in the use of helium which is evidenced by a more favorable attitude to an enlargement of the helium program, and its use has been discussed at two cabinet meetings. It is to be hoped that while Congress is in this favorable frame of mind sufficient funds will be appropriated to make the use of helium possible in practically all of the lighter-than-air craft of both the Army and Navy, provided, of course, that the condition of their gas bags will justify it.

The production plant at Fort Worth has been shut down since December 1, 1921, because of lack of funds. The outlook is not promising that funds will become available sufficiently soon to start this plant again during the present fiscal year, but it is believed that it can be used after July 1 next.

AGRICULTURAL RESEARCH

Scientists in the government service were rejoicing over a paragraph in the Agricultural Appropriation bill which provided that the maximum salary of any scientific employee should not exceed $6500, the present limitation being $4500. Their exultation, however, was shortlived, for this clause was struck out of the bill by the House on a point of order and the bill, as amended, was passed by that body on March 13.

As a result of the very generous attitude of the Department of Agriculture to encourage its workers to prepare themselves more fully for their work, an increasing number of the research men of that Department, whose headquarters are connected with educational institutions, are enrolling for graduate work in those institutions. Informal instructional courses are also being held practically every day of the week for the employees of the Department in Washington. This work consists of lecture and laboratory courses in a number of subjects in which the staff of the Department is sufficiently interested to distribute the arrangement of such courses.

COMMITTEES NAMED

The National Research Council has appointed a committee to investigate the properties of ammonium nitrate. The personnel of the committee is as follows: C. E. Munroe, National Research Council, *Chairman;* S. P. Howell, representing the Bureau of Mines; R. C. Tolman, representing the Department of Agriculture; C. G. Storm, representing the Ordnance Department, United States Army; C. P. Beistle, representing the Bureau of Explosives of the American Railway Association; and C. A. Bigelow, representing the Institute of Makers of Explosives. It is expected that the Navy Department will also be represented on this committee. This committee has been appointed because of the constantly increasing importance of ammonium nitrate in various fields.

Upon the request of W. D. Bancroft, the National Research Council has appointed the following Committee on Theory of Reactions of Nonelectrodes: Julius Stieglitz of the University of Chicago; Roger F. Brunel of Bryn Mawr; H. S. Fry of the University of Cincinnati; L. W. Jones of Princeton University; James Kendall of Columbia University; G. N. Lewis of the University of California; and W. A. Noyes of the University of Illinois.

The Office of Industrial Hygiene and Sanitation of the Public Health Service is making a study of brass foundry ague, following up the suggestion of Professor Lehmann that the fever is due to zinc, and is studying the effect of the fumes of volatile zinc on the lower animals. Thus far the work has consisted of determining the zinc in the food of normal animals and its distribution through the various body tissues. It is contemplated later to expose the animals to brass and zinc fumes and if it is then found possible to produce ague in the lower animals an attempt will be made to determine the method by which the poison causes the disease and whether zinc is responsible for it.

The same office also has under way a study to determine the per cent of efficiency of the Palmer test machine in various types of dust.

The Bureau of Mines, at its Pittsburgh Experiment Station, has under way an investigation to determine the cause of gum formation in gasoline in storage. It is estimated that the investigation may occupy two years.

The New Orleans Association of Commerce has requested the assistance of the Bureau of Mines in an educational campaign looking toward the abatement of the smoke nuisance in that city.

The Tariff Commission has begun an investigation to bring up to date the information which it gathered some time ago on chemical and optical glassware. As soon as the investigation is completed the results will be published by the Commission.

Senator Frelinghuysen has introduced a bill which, if it becomes law, will transfer the Tariff Commission to the Department of Commerce. The indications, however, point strongly to the fact that the bill will never become law.

March 13, 1922

LONDON LETTER

By Stephen Miall, 157 Haverstock Hill, Hampstead, N. W. 3, England

Those of us who live in London are apt to speak and even to think of it with some not very pronounced measure of disparagement. Those who were born here, because this depreciation is a habit, a sort of pride which makes it unnecessary to praise our metropolis. If I take a visitor to see Gray's Inn or the Temple Church I feel that no observations of mine are needed; if the visitor has a soul he will at once think as I do; if he has none I am sorry for him and must enjoy the spectacle myself. And those who come from the provinces and are merely sojourners here have their affections firmly established in Devon or Yorkshire or whatever other place colored the vivid and undying impressions of infancy. But in this week we have had in London three first-class chemical lectures, and there is no other place in the Empire and not many in the world where this could happen in the normal course of things without the accident of a congress or the deliberate effort of some organizing secretary. The three lectures I have in mind—and there may be others—were one by Dr. E. F. Armstrong before the Society of Chemical Industry on the principles of catalysis, a paper distinguished both by clear thinking and clear speaking; the second by Mr. E. V. Evans before the Society of Arts on some problems of the gas industry. This or something like it was its title, but it was in fact a chemical revue in which the lecturer was by turns, or all at once, chemist, artist, and comedian. The point which the man in the street laid hold of was that tobacco smoke contains both prussic acid and carbon monoxide, the latter in appreciable quantities. Think of this when you smoke tobacco! Prussic acid in minute doses is a valuable tonic; small quantities of prussic acid are necessary for the fattening of cattle—so it is said—and probably the virile characteristics of the Red Indians from whom we learned the art of tobacco smoking were due to the stimulating effects of the prussic acid they inhaled. The third lecture was by Sir Ernest Rutherford on disintegration of the atom, delivered nominally to the Chemical Society, actually in the spacious hall of the Mechanical Engineers and to the first four or five hundred people who were fortunate enough, by promptness or favor, to obtain admission. The modern views of the atom were explained by the man who, in this country, knows the subject better than anyone else, who was lucid and easy to follow and has a voice that a sergeant-major might envy. One is always a little uneasy when a physicist begins his oration; he is apt to break off and interpolate a few remarks on Fourier's theorem and then turn to a blackboard and "scrawl hieroglyphics alarming" as a Scottish poet hath it. But this lecture was entirely free from stunts of this nature and if this excellent example is followed I shall abandon my projected Society for the Prevention of Cruelty to Chemists and the Association for the Discouragement of the Integral Calculus.

The Society of Chemical Industry has had a memorable year. The visit to America gave some of its members not only a delightful holiday but provided them with ideas and time to turn them round in the gruel which chemists call their brains. The writer has no pretension to be a chemist. "Je ne suis pas la rose mais j'ai vécu près d'elle." This is the first outstanding feature; the second is that the late Dr. Messel, famous for his work on the contact process for the manufacture of sulfuric acid, left the Society a sum of £20,000 and this has placed it in some security. On reading this sentence through I find it is rather ambiguous, but both interpretations are correct. The Society in recognition of Dr. Messel's achievements in applied chemistry and probably (if we could get at the back of our Treasurer's mind) with a vague hope that Lord —— or Sir —— or Dr. —— will be encouraged to do likewise, has instituted a Messel Memorial Lecture to be given every two years by some one who has rendered signal service by research or in some other manner to industrial chemistry. The first lecture is to be delivered next summer by Prof. H. E. Armstrong who has announced a long Greek title to it, partly, I suppose, because he has always scoffed at the classics and now wishes to do the unexpected, and partly to shock the chemical world and dislocate them out of their well-worn rut. The sculptor, Mr. Gillick, an artist of repute, is now engaged in designing a medal to be given to the lecturer and to perpetuate the researches of Dr. Messel, his generosity to the Society of Chemical Industry, and the other considerations concerned in the grant of the medal. If these are artistically planned and compressed into a circle two inches in diameter the close-packing theorem of Pope and Barlow will have a formidable rival.

The Society has had a successful year and has a surplus of some $18,000 of revenue over expenditure. It has, therefore, abolished the Finance Committee, a characteristic English procedure. But one is sorry to find that the current year is feeling the effects of bad trade and the advertisement revenue has now begun to decline. When he thinks, good easy man, his greatness full surely is a-ripening, the manager brings a long list of firms who propose to curtail their advertisements. During the last year the Chemical Society and the Society of Chemical Industry have hatched out a scheme for joint meetings in the provinces. If this effort of coöperation is successful I suppose some joint meetings in London could be attempted. In time we shall effect a reunion between the pure and the applied; they have not been divorced, only separated.

February 18, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

In my last letter, I discussed efforts which are being made to obtain copyright for inventors, and especially for chemists.

In addition to the points which I mentioned, the following resolution has been passed, that *"un droit d'auteur á dèfinir* ought to be granted to scientists for their discoveries which are used in the industries, as well as to inventors after the expiration of their patents. In the public interest, one part of this copyright fee should go to a central depository for the profit of scientific research, the organization and development of laboratories, grants to scientists, and help to the young in their scientific development."

The Société de Chimie Industrielle ratified all decisions at its February 22 meeting. The plan is to be defended before Parliament by Mr. Barthelmy, deputy and professor in the Faculté de Droit of Paris, and by President Viviani.

The idea of collecting from the copyright a portion to be used for the maintenance of industrial research laboratories is of special interest. In the preliminary discussion a typical example was offered by Mr. André LeChatelier, brother of Professor LeChatelier.

Mr. André LeChatelier, who is the director of an industrial research laboratory modeled in miniature on the Mellon Institute, stated that the laboratory had developed a process for extracting peanut oil in 50 to 60 per cent yield, while the daily yields of the Marseilles industry, the center of French peanut-oil extraction, reached only 40 per cent. This work constituted an invention and a distinct improvement. Mr. LeChatelier stated that he had been unable to obtain from the manufacturers the payment of a fee which was perfectly legitimate on account of the development of their business.

Along the same line, Mr. Sabatier, whose work on catalysis and hydrogenation has created new industries, says in humorous fashion that the only profit which he has obtained from his work consists of a package of candles which were offered to him by a manufacturer of hydrogenated oils.

PROFESSOR LECHATELIER'S JUBILEE

On January 23, French chemists gathered about Mr. Henry LeChatelier, whose scientific jubilee they celebrated, and to whom they presented a gold medal in honor of his work.

A pupil of Sainte-Claire-Deville, it may be said of Mr. LeChatelier that his work marks a decisive step in the progress of chemistry. His early work on hot air, on lime and cements, on the rate of combustion of gases, on alloys, on metallography, on the measurement of high temperatures by means of the thermoelectric couple prepared him wonderfully for the theoretical studies which form the culminating point of his work. The application of Gibbs' mathematical ideas to thermodynamics led him to the formulation of the rules of chemical mechanics which are now the basis of all research and all chemical education.

There is no need to dwell on the importance of this work or to eulogize the great chemist who for fifty years has contributed so much to the progress of the science. Many great, modern industrial discoveries have had their germ in the work of Mr. LeChatelier. For example, the question of the synthesis of ammonia by the use of hyperpressures is derived to a large extent from the ideas expressed by Mr. LeChatelier more than twenty years ago, on the role of pressure in chemical reactions.

Since the subscription for the medal more than covered its cost, the remainder (more than 100,000 francs) has been placed at the disposal of the Académie des Sciences for the creation of a bureau of scientific research applied to industry.

AMMONIA SYNTHESIS

Research on details is perfecting the ammonia synthesis. Mr. Decarriere has shown the extremely toxic effect of phosphine on the catalysts. One-fifty-thousandth of one per cent of phosphine destroys the catalyst as rapidly as 2 per cent of hydrogen sulfide.

Mr. Claude reports the difficulties which he has met in cooling his apparatus. The formation of ammonia at high pressures sets free a considerable quantity of heat, and in his earlier experiments Mr. Claude used fused lead as a cooling agent. Although the tubes in which he carried out the reaction were very thick, they cracked from the outside inward, because of the fact that the amount of heat evolved in a given time could not be absorbed sufficiently rapidly by radiation. Mr. Claude was next led to insulating the tubes thermally by surrounding them with kieselguhr. This thermal insulation makes possible an even distribution of heat from the tube.

Messrs. Matignon and Frejacques have studied the formation of urea from ammonia, or rather from ammonium carbamate. The advantage of urea over ammonia is that the same amount of nitrogen is contained in a much smaller volume. The processes described give hope of the rapid development of great facilities for the conversion of ammonia to urea.

ANTI-OXIDATION CATALYSTS

Since his return from America, Mr. Moureu has resumed the direction of his laboratory and has just published an interesting piece of research which has been going on for some time, on anti-oxidation catalysts. With Mr. Dufraisse he has established the fact that a number of substances possess a power which he calls "anti-oxygen." Numerous compounds, especially unsaturated compounds, oxidize rapidly in the air. Messrs. Moureu and Dufraisse have found out that certain substances, in general, phenols, prevent this autoxidation, and that infinitesimal doses of the phenols are sufficient to cause the phenomenon. This anti-oxygen phenomenon is therefore a catalytic action.

As an example, one molecule of hydroquinol prevents the spontaneous oxidation of 40,000 molecules of acrolein.

This conception of anti-oxygen substances may be very fruitful, especially in biological chemistry, where oxidation (both *in vitro* and in the organism) may be conditioned by the presence of these anti-oxygen phenolic compounds, which are very numerous in the organism.

From the industrial point of view also, linseed oil, which everyone knows is a markedly drying oil, remains fluid (even when spread in thin layers) on long exposure to the air, when a trace of an anti-oxygen compound is added. Butter mixed with an anti-oxygen in catalytic doses no longer becomes rancid.

CATALYTIC OXIDATIONS

In the field of oxidation, Mr. Jaloustre has demonstrated the oxidative power of thorium X. Very small amounts of thorium X oxidize adrenalin and morphine very rapidly. The oxidations are much stronger than those obtained with the manganese salts which act as catalysts in oxidation. This work is part of an interesting effort to connect catalytic action with radioactive phenomena.

RADIOACTIVE COMPOUNDS

Messrs. Lebeau and Jolibeau have both been studying the oxides of uranium. These oxides have been described in large number, as a result of the fact that they form solid solutions one with another. In reality, there are only three perfectly distinct oxides: UO_3, U_3O_8, and UO_2.

Mr. Barlot has used uranium and sodium salts for the differentiation of the fatty acids. A crystalline salt of uranium and sodium is formed by the acids containing a number of pairs of consecutive carbon atoms. Thus, with formic and propionic acids no salt is formed, but the well-crystallized salt is obtained with acetic, butyric, etc., acids.

I have already mentioned the discovery of radium minerals in the Belgian Congo, in the Katanga region. It appears that these minerals are very rich in radium and have a content greater than the carnotites of Colorado. Moreover, the minerals lie near the surface of the ground. A factory with an annual production capacity of 30 grams is now being built at Katanga. This figure seems rather high, for if it is reached a serious disturbance of the radium market will result.

February 23, 1922

The Belgian geologist, Professor Scouppe of the University of Ghent, has just returned from the Belgian Congo where he located two radium deposits, said to be the richest in the world. Professor Scouppe christened the mineral "Curite." The Belgian authorities have started the construction of a plant near Antwerp, which it is said will produce one gram of radium from nine tons of the mineral.

Personals

Mr. C. S. Brinton has been appointed Chief of the Philadelphia Food and Drug Inspection Station of the Bureau of Chemistry, effective March 1, 1922. This appointment is made to fill the vacancy caused by the transfer of **Mr. Arthur Stengel** to the Bureau of Chemistry in Washington.

Miss Hannah L. Wessling has resigned her position with the Department of Agriculture in order to accept that of Home Economics Consultant with the Northwestern Yeast Co., Chicago, Ill. For a number of years Miss Wessling was District Field Agent with the States Relations Service specializing along the line of flours and baking.

The company of Jayne and Sidebottom, Inc., recently formed in New York with offices in the Whitehall Building, 17 Battery Place, represents manufacturers as agents for the sale or purchase of materials generally classed as chemicals for the textile, paint, rubber, dye, chemical, pharmaceutical, paper, leather, and allied industries. Previously **Mr. Jayne** was manager of The Barrett Company Plant at Frankford, Philadelphia, and **Mr. Sidebottom** was manager of the Technical Service Department of the same company.

Mr. Thorwald A. Carlson until recently employed as chemist by the American Smelting and Refining Co., at East Helena, Mont., has now become a member of the technical staff at the Forest Products Laboratory, Madison, Wis.

The Pittsburgh Testing Laboratory announced at its annual meeting held in Pittsburgh, on February 2, 1922, the retirement of its president, **Mr. Geo. H. Clapp**, his reappointment as a member of the board of directors of the company, and the election of Col. James Miliken to the presidency of the company.

Mr. Odus C. Horney has been relieved from duty as Ordnance Officer of the 8th Corps Area, Fort Sam Houston, Texas, and assigned to the command of the Frankford Arsenal, Philadelphia, Pa.

Maj. J. K. Clement has been relieved from duty as Commanding Officer at the U. S. Nitrate Plant No. 2, Muscle Shoals, Ala., and assigned to duty in the office of the Chief of Ordnance as a member of the Ordnance Salvage Board.

Mr. A. P. Gest, Jr., formerly with The Barrett Co., is now associated with Keator & Wilson, Philadelphia, Pa., as sales engineer.

Mr. A. C. Grubb received his Ph.D. degree at the University of Chicago last June and is now occupying the position of assistant professor of chemistry at the Univ. of Saskatchewan.

Mr. Albert MacLeod, formerly with the H. J. Heinz Co., Bay City, Mich., is now with the Sherwin-Williams Co., as their assistant azo dye chemist.

Mr. Arthur D. Holmes, who has been research chemist with the E. I. du Pont de Nemours & Co. at the Jackson Laboratory, has resigned to accept a position with the E. L. Patch Co., Boston, Mass., to establish a research laboratory which will be concerned with investigations along biological and physiological lines.

Mr. F. E. Dodge, formerly with The Barrett Co., is now vice president of the Protexol Corporation, and is manufacturing manager of their New York plant.

Mr. C. L. Bryden, formerly with the Kelly Filter Press Co., is now eastern representative for the Vallez Rotary Filter Press, New York, N. Y.

Mr. L. E. Roberts has resigned his position as assistant director of research, American Writing Paper Co., Holyoke, Mass., to become physical chemist with the Bureau of Mines, Pacific Coast Experiment Station, Berkeley, Cal.

Mr. Gustave E. Behr, Jr., resigned his position as superintendent of Balder, Adamson Co., of Philadelphia, Pa., and is now engaged in a special investigation for the National Lead Co., at their main chemical laboratory, Brooklyn, N. Y.

Mr. Hugh M. Henton has given up his position as instructor at Case School of Applied Science, to open an office in the National City Building, Cleveland, Ohio, and further industrial research in metallography and kindred branches.

Mr. Hollis H. Dann, recently chief chemist at Central Fe, Cuba, has become associated with the Darco Corporation of Wilmington, Del., as Technical Assistant to the Sales Manager. Mr. Dann will have charge of the development work in connection with the cane sugar industry.

Mr. Charles F. Hobson, formerly general manager of the Westchester Chemical Co., of N. Y., is now general manager of the Wamesit Chemical Co., Lowell, Mass.

Industrials

Construction work is to be started immediately upon a distillery at Anaheim, Cal., to be built by the Anaheim Sugar Company for the utilization of molasses in the manufacture of alcohol. The latest improved Barbet system is to be installed, and the distillery is planned to have a capacity of 25 tons of molasses in 24 hrs. The output of the company will be sufficient to keep the distillery in operation during the entire year.

The majority stockholders of the Redmanol Chemical Products Co., of Chicago, have purchased a majority interest in the Condensite Company of America, Bloomfield, N. J.

A new plant is now being erected near Marshall, Tex., for the production of Darco, which is a new refining, purifying, deodorizing and decolorizing carbon. In designing the plant particular attention was paid to the efficient handling of materials, and from raw material to finished product the material will be handled by mechanical conveyors of the most modern design and in many instances specially designed for the purpose. It is expected that the plant will be in operation in the early spring of 1922. As an aid to manufacturers in the solution of their decolorizing and refining problems The Darco Corporation, which is controlled by the Atlas Powder Company, has recently completed a new research laboratory at its headquarters in Wilmington, Del.

The Industrial Chemical Laboratories, affiliated with the Oakland Copper & Brass Works, have been established in Oakland, Cal., under the direction of Dr. Theodore W. Doell, who was formerly connected with the du Ponts and other eastern interests. The laboratories will be devoted to consulting, research, and analytical work, and will fill an urgent demand for an institution of that character, particularly in the canning and packing field.

The U. S. Circuit Court of Appeals, Second Circuit, N. Y., tendered an opinion on February 14, 1922, affirming a decision previously handed down by the Federal Court at Buffalo, N. Y., sustaining a patent owned by The Permutit Company covering zeolite water softeners. According to this decision all zeolite water softeners on the market not manufactured by this company are an infringement of this patent.

Messrs. J. T. Donald & Co., Ltd., chemical engineers and consulting chemists of Montreal, have removed to new and larger premises which they have purchased and specially equipped for their laboratory and consulting work.

The United States Cast Iron Pipe and Foundry Company has opened a new office at the Interstate Building, Kansas City, Mo.

The Weller Manufacturing Co., Chicago, Ill., has perfected a portable reciprocating feeder to take care of materials received in hopper bottom cars. This feeder eliminates the digging of pits and cars can be unloaded at a point most convenient to where the materials are required. The machine operates above the track, is mounted on roller bearings, and can be easily slipped under the car. It will handle sand, stone, gravel, coal, ore, etc., and requires only one man for its operation.

A patent covering an apparatus for the recovery of gasoline vapors from natural gas, casinghead gas, refinery and tank farm vapors, has just been granted to the Gasoline Recovery Corporation, as assignee of G. A. Burrell, G. G. Oberfell, and C. L. Voress. The apparatus consists of drums, filled with activated charcoal and connected on one side to a steam boiler and on the other to gasoline condensers. In commercial operation the gasoline-bearing gas is allowed to flow through one of the drums of charcoal where the gasoline is absorbed and retained, the balance of the gas passing through unchanged. Steam at low pressure is later used to drive the gasoline from the charcoal. Three commercial plants have already been built.

The Bureau of Foreign and Domestic Commerce, in coöperation with the Bureau of Mines, has just completed arrangements to produce in this country motion picture films showing methods of production and employment of American machinery and similar products. The actual cost of the photography, as well as the expenses incurred in the making of additional prints of the films, is borne by the coöperating company. After the picture has been completed and approved, the work of distributing the films, both in this country and abroad, is taken care of by the Bureau of Foreign and Domestic Commerce without any further expense to the coöperating company. It is possible to give a very close estimate as to the cost of producing such a film, and arrangements can be made for the government engineer to visit the plant for this purpose.

BOOK REVIEWS

Cane Sugar. By Noël Deerr. 2nd revised and enlarged edition. viii + 644 pp. Norman Rodger, 2 St. Dunstan's Hill, London, E. C. 3, England, 1921. Price 42s. net.

In the reviewer's opinion this is in many respects a very remarkable book, one of the best of the type of which we have too few examples, combining scholarship, technical knowledge, and readability to an unusual degree. It is so great an improvement over the already excellent first edition and contains so much new material that it should be in the hands of all men interested in sugar technology. The section dealing with the origin and development of the sugar cane shows an enormous amount of patient research. The rather vague statements found in existing literature and the difficulty of sifting out the truth from a mass of hearsay evidence made the task hard, but it has been admirably accomplished. In the sections on agricultural and on mechanical engineering, both the methods and the machinery described conform thoroughly to present-day standards. This also may be said of the section on chemical engineering and sugarhouse practice wherein both the chemical and the engineering features are properly blended, making the treatment exceedingly clear and easily understood both by chemists and engineers. The strictly chemical side of the book is, in the main, analytical, and has been brought thoroughly up-to-date. The final chapter on fermentation, although brief, is satisfactory.

Among the noteworthy features of the book are the historical developments given of the various machines and the careful treatment from the mathematical side of what is known as chemical control. This latter is too often done in a rule-of-thumb fashion. Deerr's logical and sound methods should be studied by all chemists interested in sugarhouse practice.

The book, of course, in no wise replaces some of the standard books in sugar literature such as Browne, Spensor, and Prinson-Geerligs. It gives few analytical tables, and the description and criticism of methods are meant for the chemist rather than for the beginner, and for the engineer rather than for the mechanic. Sometimes, perhaps, this tendency is carried too far. Under the head of polariscopes, for instance, Deerr discusses only principles and deliberately leaves out specific instances. In the writer's judgment the description of principles here is too brief for the average chemist to make much use of and the section could have been improved by the description of a modern polariscope. This is a matter of opinion, and Deerr has deliberately left this field to such books as those of Browne and of Landolt.

These points, however, are of minor consequence. The book as it stands meets admirably a pressing demand, is well printed on good paper, and is a valuable contribution to chemical technology.

C. E. Coates

Bleaching. By S. H. Higgins, M.Sc., Head of Research Department, Bleachers' Association, Ltd. Economic Series, No. XVI. Publications of the University of Manchester. vii + 137 pp. Longmans, Green & Co., New York; University Press, 12 Lime Grove, Manchester, England, 1921. Price, $3.75.

We have known S. H. Higgins for many years as a writer on bleaching and allied textile subjects, and consequently welcome this latest publication. As stated in the preface, "The idea of this volume is not to give an account of the subject of bleaching, but to act more as a supplement to other published works, dealing with this branch of chemical industry. It is not meant for those who have no other books on bleaching. The principal intention of the author has been to discuss the important researches which have been published during the period 1908–20, bearing on the bleaching industry, and to present a record of work as a basis for the extension of research in the industry."

The book is divided into sixteen chapters in which the subject is subdivided and arranged in logical sequence. After the introduction follows a chapter on the constituents of vegetable fibers, which includes the waxes, proteins, mineral, pectic, and coloring matters which are incorporated with the cellulose. The formation and characteristics of these constituents during the growth and maturity of the fiber are discussed as far as our present knowledge permits.

In the several chapters which follow, on the elimination or separation of the noncellulose constituents from the parent fiber, many valuable data and many abstracts are given which embody the underlying principles of scouring and bleaching upon which our modern practice is based. In the chapters on the reactions of cellulose with water, acids, alkalies, and oxidizing agents, the discussion develops the conditions under which these agents are safely employed, as well as the conditions under which costly faults and destruction of the fiber result. Several chapters on fermentation, bleaching processes, faults, etc., complete the scope of the book.

We consider the book a valuable addition to the present literature relative to the subject of bleaching. The bleacher's chemist will find in it many facts which confirm his experience and many others which are full of suggestions for improvements in present methods.

Fred H. Webster

Technology of Cellulose Esters. By Edward Chauncey Worden, Ph.C., B.S., M.A., F.C.S. Volume I, in 5 parts. Part 1—cxxv + 664 pp.; Part 2—cxvii + 902 pp.; Part 3—cxvii + 810 pp.; Part 4—cxvii + 710 pp.; Part 5—623 pp.; 296 illustrations. D. Van Nostrand Co., New York, 1921. Price, $40.00.

"The aim of this work is to present the entire subject of the combinations of normal and modified cellulose with the acidyl and alkyl radicals in such completeness, clarity, accuracy and detail, that inability to locate the information desired in the collective indices will be trustworthy evidence that the matter sought was either ephemeral, irrelevant, inaccurate, nonexistent, or valueless."

The above excerpt from the preface of Volume I here under review is explanatory of the scope of the contemplated ten volumes, of which Volume VIII on the "Carbohydrate Carboxylates" (cellulose acetate) was published in 1916.

The general schematic arrangement of Volume I is excellent, but the subtopics are not always so well arranged. Many grammatical errors are apparent, and in several places for many consecutive pages, the manifold references obliterate all but a single line of the text.

Considerable matter seems irrelevant, but since the author recognizes that such may appear to be the case and expressly requests that criticism on this score be withheld until the entire work is completed, it is quite proper to accede to this request.

An excellent feature worthy of mention is each individual part (exclusive of the index) of the complete table of contents of the entire volume.

While Volume I, consisting of five books, is more or less comprehensive in itself, it is in a sense introductory to the nine volumes which are to follow (Volume VIII already issued) and which are to deal in more elaborate detail with the industrial applications of cellulose compounds and esters.

Of Volume I, Part 1 covers in four chapters the subjects of cellulose, starch, cotton, and the preparation of cotton for esterification. There is much theoretical and much practical information on these topics, with ample bibliography to satisfy the most inquisitive.

Part 2 deals in four chapters with nitric acid, sulfuric acid, mixed acids, and acid tables. It goes exhaustively into the raw materials, manufacture, properties, analyses, handling, etc., of these nitrating acids, brings the data fairly well up to date, and by itself is a useful book, although naturally of more value to the cellulose nitrate producer.

Part 3 covers in three chapters nitrocellulose theory, nitration of cellulose, and analytical determination of the cellulose nitrates. The first chapter is much more inclusive than its title indicates, for it outlines the history of cellulose nitrate, imparts some information on various nitrated carbohydrates and resins, and gives in considerable detail the layout and construction of a modern guncotton plant. This last perhaps might more appropriately have been included in the chapter on the nitration of cellulose, in which chapter we are pleased to note the author departs at times from the bibliographic style and imparts some of the useful technical information apparently acquired from his extended experience in the cellulose ester field. The last chapter on analysis and specifications is comprehensive.

Part 4, on the historical development of the cellulose esters, discusses solvents, camphor and its substitutes, and the various industrial applications of cellulose esters with some amplification along pertinent and correlated subjects. It is in reality an elaborated synopsis of what is to follow in more detail in the succeeding volumes.

Part 5 is the index to the other four books. It includes a complete index of patents, as well as an index to subjects and an index to authors. The fact that it comprises 623 pages speaks for itself as to its thoroughness and painstaking and arduous preparation.

When we consider that the field of cellulose chemistry has probably been only scratched, that no one has really collected heretofore, in a work of any magnitude, the large mass of detached data which have been published on the subject in its present state of development, the value of Dr. Worden's contribution easily becomes apparent. The task he has set for himself is a life work. Few would have courage to undertake it.

H. S. MORK

Elementary Chemical Microscopy. By EMILE M. CHAMOT, Professor of Chemical Microscopy and Sanitary Chemistry, Cornell University. xv + 479 pp. 2nd edition. John Wiley & Sons, Inc., New York, 1921. Price, $4.25.

The first edition of this work was published in 1915. While intended primarily as a textbook, it collected in one place data on microscope apparatus, optical-crystallographic methods, and characteristic reactions of the common elements in such a useful form that no reference library directed toward solving chemical problems could be considered complete without it.

The preface to the second edition points out the increased recognition of the usefulness of the microscope in the chemical laboratory, brought about especially by the scientific activities connected with the prosecution of the recent war. Since, however, the progress has been not so much in the development of new methods as of new applications of old ones, the plan of the first edition has been retained. Illustrations of crystals obtained in the various tests, and other data appropriate to a reference manual, are accordingly still omitted, although the welcome news is given that the author has a handbook in preparation in which such matter will be included. The second edition differs from the first in some rearrangement of chapters and rewriting of paragraphs, with the addition of a few data on new apparatus and procedures.

The book contains much useful information as to microscopes, accessories, and laboratory equipment. Methods of measurement under the microscope are described in detail, with special reference to practical applications. Quantitative analysis by the microscope is shown to be possible in various fields. The value of refractive index data for identification of substances is well emphasized. Lists of immersion liquids are given; although the usefulness of oils of the type of "liquid petrolatum" in making them up is not mentioned. The lists of indices of crystalline compounds also seem susceptible to improvement. More than a third of the book is given over to the methods of microchemistry in the usual sense—operations with minute quantities of materials and qualitative analysis by obtaining characteristic crystalline compounds.

It would appear that no wide-awake chemist could afford to be without access to Chamot's "Chemical Microscopy."

EDGAR T. WHERRY

Laboratories: Their Planning and Fittings. By ALAN E. MUNBY, M.A., F.R.I. 220 pp. 165 figures. 8vo. D. Van Nostrand Co., New York, 1921. Price, $6.00.

The author has added a well worth while volume to this too little discussed subject. While the requirements of chemistry, physics, biology, and geology are all considered, the major part is concerned primarily with the needs of chemical laboratories devoted to teaching. No attention is given to the peculiar needs of industrial chemical or other laboratories.

One welcomes with much interest the numerous floor plans of laboratory buildings, floor plans of 19 English and 8 foreign laboratories being figured.

Because Mr. Munby is English, the book necessarily is largely a description of British school and university laboratories. The author apparently has not had available for close study the new extensive and modern laboratories built in Holland, Germany, and America. To one familiar with the advances in laboratory construction in America, it comes as a shock to have advocated the putting of the hoods ("fume cupboards") in the windows, benches instead of tablet arm chairs in class and lecture rooms, and waste pipes in troughs in the floor, but in spite of these and a few other similar statements the reviewer wishes to express his appreciation of the sane, clear, and valuable discussions of many problems of laboratory design and equipment and to urge all those having the planning of laboratories to read the volume with care.

RALPH H. MCKEE

Bleaching and Related Processes. By J. MERRITT MATTHEWS, PH.D. 676 pp. 300 illustrations. The Chemical Catalog Co., Inc., New York, 1921. Price $8.00 net.

Because of his extensive experience as a textile chemist, and particularly because he has specialized to a considerable extent as regards cotton bleaching, the author is especially well equipped to write an authoritative book upon this subject. Combining his own first-hand knowledge of the subject with the most reliable information and data to be obtained from the general literature, he has succeeded in bringing together in one volume the most comprehensive and exhaustive treatise upon this branch of textile chemistry that has thus far appeared in English if not in any other language.

The arrangement of the text is such that one may find a continuous and complete discussion of the preliminary treatment and bleaching of the common textile fibers. As would naturally be expected from the relative importance of cotton bleaching, by far the larger portion of the book is devoted to this fiber. The last one hundred pages are devoted to the testing of the various chemicals and materials used in the processes described and will prove a valuable reference guide to chemists engaged in bleaching, scouring, and finishing plants.

The subject matter is excellently illustrated, and while the writer specifically states in the preface that he has purposely omitted the dry details of mechanical description in regard to these illustrations, there are instances where a little more detail would have undoubtedly been of interest to seriously minded readers and students.

At the end there will be found an excellent bibliography and a comprehensive index.

The volume should form a valuable addition to the working library of every textile chemist and bleacher.

Louis A. Olney

Metallurgy of Zinc and Cadmium. By H. O. Hoffman. 341 pp. McGraw-Hill Book Co., Inc., New York, 1922. Price, $4.00.

Professor Hoffman's famous books on the metallurgy of lead, copper, and general metallurgy naturally pave the way for the keenest interest in his latest treatise, and the very great need of the zinc industry for an up-to-date treatise could not have been filled better than by this illustrious author.

The first few chapters of the book are given over to the physical and chemical properties of zinc; as a metal in commerce, including its impurities and their effects; as used industrially for alloys and protective coatings; as zinc compounds and their industrial use. The very thorough manner in which Professor Hoffman has described the properties of zinc, supplemented by a complete reference to original articles, will make this section of his book a most valuable reference to that host of chemists and metallurgists who each generation attempt to find new methods of smelting and refining zinc.

The next several chapters, preceded by a short description of the character of ores, describe in Professor Hoffman's well-known detailed style the metallurgical processes and equipment used for the smelting of zinc ores. The basic chemical reactions involved in calcining, roasting, distillation, and refining are explained so clearly that the works manager or superintendent will find reference to this book a scientific explanation and guidance to the solution of those numerous perplexing plant problems so frequently confronting him. Likewise in the description amplified by numerous drawings and photographs, of construction and operation of the metallurgical equipment, the same thorough attention to basic principles has been given, including in sufficient detail the furnaces and processes of former years both in the United States and Europe, as to trace the evolution of improvement to present-day equipment and practice, and give the reader a thorough understanding of the operations.

The short description and references to apparatus and processes, *e. g.*, blast furnace and electric furnace smelting, which have been tried and so far prove a failure commercially, add materially to an understanding of zinc metallurgy.

A very complete chapter occupying some fifty pages is given to description of the new process of electrolytic recovery of zinc from ores which has developed from imperfect laboratory experiments to a vast commercial industry in the past ten years. The basic principles of electrolysis of zinc solution, together with the special features of roasting and purifying the leach liquor preparatory to electrolysis, are given in detail. Numerous drawings, photographs, and flow sheets make clear the commercial operations at Great Falls, Montana, and other plants.

A short chapter on zinc oxide covers the more essential points of its manufacture and marks the progress of development in this branch of the industry. The short period since this branch has expanded has not permitted details of processes and practice to become generally available for the author's use. The section on cadmium is complete in its description of the properties, uses, and recovery of cadmium as commercially known.

The generous references to other authors' publications giving further detailed description of scientific investigations, plant operations, and commercial aspects of the zinc industry are a further valuable part of this book. It is unfortunate for many of those engaged in the zinc industry that they could not have the benefit of Professor Hoffman's precise description of the basic principles and processes of manufacture of sulfuric acid and producer gas which are a part of many zinc smelting works; but as a treatise on strictly the metallurgy of zinc and cadmium, all those interested in zinc will find this book profitable to read for a clear and better understanding of zinc industry and a valuable reference for accurate information on zinc metals and compounds.

L. E. Wemple

Elements of Fractional Distillation. By Clark Shove Robinson. 205 pp. McGraw-Hill Book Co., Inc., New York, 1922. Price, $2.50.

The author states in this book that the principles of fractional distillation are explained according to the ideas of physical chemistry and chemical engineering. The book is divided into five parts. The first part deals with fractional distillation from the standpoint of the phase rule. The second part discusses some of the quantitative aspects from the standpoint of the chemical engineer. Part three discusses the factors involved in the design of distilling equipment. Part four gives a few examples of modern apparatus, while the last portion includes a number of useful reference tables.

As a person reads the book, he is struck by the fact that here is a very able and new presentation of a subject which is vital to many industries to-day. There is no other book, at least in the English language, which covers the subject in such a thorough manner. The principles involved in fractional distillation, and all the various rules, laws, and equations are mathematically explained and practically illustrated. The various chapters treat of the phase rule, one component systems, two component systems, more complex systems, the gas laws, solutions, concentrated solutions, simple distillation, fractionation, rate of fractionation, discontinuous distillation, design of a discontinuous still, the fractionating column, the condenser, accessories, continuous distillation, ammonia, benzolized wash oil, methanol, ethyl alcohol, and an appendix of tables.

It will be observed that one is led from theory to practice and, in the latter presentation, the author has drawn upon his former experience with the E. B. Badger & Sons Company for practical data. Some published and unpublished data of W. K. Lewis and experimental work of the Massachusetts Institute of Technology are also presented.

The theoretical side of fractional distillation is well presented, and the laws applied to distillation problems in a few industries where distillation is on a fairly sound basis. The author states that another book will follow dealing with the general practice of fractional distillation and its application to the several industries. It is to be hoped that one of the industries to be treated will be the petroleum industry.

The author writes lucidly, and happily, not only from theoretical knowledge, but apparently also from a considerable practical knowledge of his subject.

G. A. Burrell

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

February

A very comprehensive report on the Argentine **petroleum** industry which has been compiled by the United States Embassy in coöperation with the commercial attaché at Buenos Aires may be consulted in the Bureau of Foreign and Domestic Commerce. (P. 323)

The **potash** situation in Poland is reviewed. (P. 341)

A new high **explosive** called **brazilite** is reported to have been discovered in Brazil. In experiments this explosive resisted without deflagration all mechanical and chemical tests, and it is claimed that the explosive does not give off gas prejudicial to the operator and is said to be of extra good quality. (P. 346)

An inspection of bleached **wood pulp** in the State timber yards of New South Wales, Australia, reveals the likelihood of a generous supply of newsprint for Australia from home sources. This pulp is made from mountain gum which had hitherto been considered of small commercial value. (P. 348)

A report from the Vice Consul at Singapore is to the effect that a new use for **rubber latex** in the manufacture of paper seems to have been discovered. It is claimed for the new discovery that it will not only reduce the cost of paper manufacturing materially and simplify paper-making methods, but that it will greatly improve the quality of the product. (Pp. 376–7)

It is reported that the Forestal Land, Timber, and Railway Company has secured control, by purchase, of the majority of the shares of the widely known Rhenische Dye Extract and Tanning Company of Benrath. The *Boersen Zeitung* in commenting upon this transaction states that England having thus invested capital in the **tanning trade** must necessarily appear as a great danger to the German leather industries. (Pp. 380–1)

The use of **alcohol** as fuel by an American machine in the recent tractor demonstration at Santa Cruz has aroused much interest in Brazil and the test is reported to have been very successful. (Pp. 382–3)

The most promising **petroleum** field so far discovered in the Province of Antofagasta, Chile, is that in the pass of Siglia, near the Argentine frontier, but it remains to be seen whether the petroleum will be found in paying quantities. (P. 384)

In the following British dominions and possessions, as well as in the United Kingdom proper, a **license for importation** of all synthetic organic dyestuffs, colors and coloring matters, and all organic intermediate products used in the manufacture of such dyestuffs, colors or coloring matters, is still required to be secured by the importer: Australia, Northern and Southern Rhodesia, Cyprus, Malta, State of Kedah (Federated Malay State), British Honduras, and Gold Coast. It is claimed that in Southern Rhodesia, at least, licenses will be granted only for such dyes and dyestuffs as cannot be supplied by the United Kingdom or British possessions. (P. 396)

By the Presidential decree of December 14, 1921, the legal time periods for the protection of industrial **inventions and trademarks,** which were declared extended from August 1, 1914, to a date to be fixed after the termination of the European War, have been definitely extended by Brazil to September 30, 1922.

The **copra** market at Sydney, Australia, for the past 35 yrs. is reviewed. (Pp. 402–3)

Comparative statistics in regard to Japanese imports of German **dyestuffs,** indicating a much increased trade since January 1921, are obtainable by application to the Bureau of Foreign and Domestic Commerce for Bulletin FE 260. (P. 412)

A preparation named **Eulan F,** which is claimed to make wool moth-proof, has been produced by a German company. It is an odorless powder slightly soluble in water. (P. 464)

It is officially announced that the monopoly by the government of Switzerland on **benzine** and **"petrole"** ended March 1, 1922. Alcohol, chestnut extract for tanning, and gasoline, kerosene, and petroleum products (except benzine and "petrole") and substitutes are still under government monopoly. (P. 475)

The production and use of **fluorspar** in Japan is described. (Pp. 506–7)

British imports of refined **petroleum oils** recorded, in the aggregate, an increase in volume in 1921 but a fall in value. In spite of this decline in prices, however, the 1921 prices are still greatly in excess of those of 1913. (P. 512)

The gross output of the Baku **oil** fields during the last quarter of 1921 continued on the increase and the general conditions manifested a certain tendency toward stabilization. The total output for the year 1921 was 2,519,290 long tons, of which 668,760 tons were produced in the last quarter, as compared with 622,900 tons in the first quarter, 659,100 tons in the second quarter, and 568,530 tons in the third quarter. (P. 513)

The French Ministry of Commerce and Industry has published a notice that the government **kerosene** stocks are entirely liquidated and that consequently the provisions of the law which required importers to purchase certain percentages of their requirements from the government cease to be in force. (P. 514)

The annual report of the Minister of Finance of Bolivia to the National Congress for the year just passed contains some very interesting statements regarding **petroleum,** in which he details the concessions granted and those that have been declared void, giving the names of some of the concessionaires. (P. 514)

A translation of the new Peruvian **petroleum** law, which was signed on January 2, 1922, is on file in the Bureau of Foreign and Domestic Commerce. (P. 514)

The varied uses of **china clay** are described. (Pp. 521–2)

A decline of 55 per cent in quantity and 56 per cent in value from the previous year's figures marked the 1921 imports of **china clay** into the United States. (P. 522)

The Belgian Minister of Finance has entered chemical products, articles not specified, including dinitrotoluene, on the duty-free list. (P. 531)

The **fertilizers** produced, imported, and used in Sweden are described. (P. 537)

A translation of the provisional **mining laws** of Persia, adopted October 2, 1917, by the Council of Ministers, is on file in the Bureau of Foreign and Domestic Commerce. (P. 538)

A newly discovered metalliferous substance, possessing unusually strong solvent properties, is being prepared for commercial use in New South Wales and gives promise of the development of extensive new industries. It is a very potent combination when used as a solvent for various organic substances. It is known as **fibroferrite,** and is said to be composed of 50 per cent of ferrous sulfate, 15 per cent of oil of vitriol, 10 per cent of ferric sulfite, and several alums and sulfur compounds. (Pp. 538–9)

STATISTICS OF EXPORTS TO THE UNITED STATES

TAMPICO—(P. 322)
- Petroleum

PERSIA—(P. 347)
- Gum tragacanth

GERMANY—(P. 437)
- Wood pulp
  - Bleached
  - Unbleached
- Muriate of potash
- Colors and dyes

SCANDINAVIAN COUNTRIES (P. 441)
- Unbleached chemical wood pulp
- Bleached wood pulp

AUSTRO-HUNGARY
- Magnesite and other nonmetallic metals

ITALY—(P. 442)
- Olive oil

SPAIN—(P. 442)
- Olive oil
- Sulfur ore
- Copper ore and matte
- Iron ore
- Manganese

ARGENTINA—(P. 450)
- Flaxseed

BRAZIL—(P. 450)
- Manganese ore

SOUTH AMERICA—(P. 451)
- Copper
- Nitrate of soda

NORTHERN NORTH AMERICA—(P. 453)
- Wood pulp
- Flaxseed

AUSTRALIA—(P. 461)
- Copra

ENGLAND—(P. 522)
- China clay

MOROCCO—(P. 538)
- Coriander

SPECIAL SUPPLEMENTS ISSUED

CHILE
CHINA
PANAMA
DOMINICAN REPUBLIC
JAPAN

CURRENT PUBLICATIONS

NEW BOOKS

Assaying: A Textbook of Fire Assaying. Edward E. Bugbee. 254 pp. Illustrated. Price, $3.00. John Wiley & Sons, Inc., New York.

Atomic Theory: La Théorie de Bohr, la Constitution de l'Atome et la Classification Périodique des Eléments. E. Bauer. Price, 4 fr. 50. Jules Hermann, Paris.

Chemical Industry: Auskunftsbuch für die Chemische Industrie. Edited by H. Blücher. 11th edition. 2 volumes. 1590 pp. Price, 35s. per volume. W. de Gruyter & Co., Berlin & Leipzig.

Coal and Smoke. J. W. Cobb. 23 pp. Price 1s. Longmans, Green & Co., London.

Coal: Pulverized Coal Systems in America. Leonard C. Harvey. Revised edition. Special Report No. 1, Fuel Research Board. 117 pp. Price, 5s. net. H. M. Stationery Office, London.

Colloids: Rôle des Colloides chez les Etres Vivants. Auguste Lumière. Masson et Cie., Paris.

Distillation Principles and Processes. Sydney Young. 210 pp. 210 illustrations. Price, $10.50. The Macmillan Co., New York.

Feedstuffs: The Valuation of Feedingstuffs by Means of Chemical Analysis. A. Smetham and F. Robertson Dodd. Price, 2s. 6d. Royal Lancashire Agricultural Society, England.

General Chemistry: A Laboratory Manual of General Chemistry for Use in Colleges. William Crowell Bray and Wendell Mitchell Latimer. 72 pp. Illustrated. Price, 50 cents. Lederer, Street & Zeus Co., Berkeley. Cal.

Household Chemistry: A Laboratory Study of Household Chemistry. Mary Ethel Jones. 173 pp. Illustrated. Price, 80 cents. Allyn & Bacon, Boston.

Inorganic Chemistry: A Comprehensive Treatise on Inorganic and Theoretical Chemistry. J. W. Mellor. 2 volumes. 1065 and 894 pp. Price, £3 3s. net. Longmans, Green & Co., London.

Laboratory Manual, Arranged to Accompany the 2nd Edition of a Course in General Chemistry. William McPherson and William Edwards Henderson. 140 pp. Illustrated. Price, $1.20. Ginn & Co., Boston.

Liquid Fuel: Die Wirtschaftliche Bedeutung der Feüssigen Triebstoffe. Peter Reichenheim. 85 pp. Price, 20 M. Julius Springer, Berlin.

Materials of Construction—Their Manufacture and Properties. Adelbert P. Mills. Edited by Harrison W. Hayward. 2nd edition. 476 pp. 192 figures. Price, $4.00 net. John Wiley & Sons, Inc., New York.

Metals: The Failure of Metals under Internal and Prolonged Stress. F. S. Spiers, Editor. 215 pp. Price, 10s. 6d. net. The Faraday Society, London.

Organic Chemistry. F. von Richter. **Vol. II. Carbocyclic Compounds.** Translated from 11th German edition by E. E. Fournier d'Albe. 760 pp. Price, 35s. Kegan Paul, Trench, Trubner & Co., Ltd., London.

Organic Chemistry: Die Methoden der Organischen Chemie. (Weyl's Methoden) Vol. I. Edited by J. Houben. 2nd revised and enlarged edition. 1121 pp Price, paper, 700 M. Georg Thieme, Leipzig.

Physical Chemistry: Introduction to Physical Chemistry. James Walker. 9th edition. Illustrated. Price, $4.50. The Macmillan Co., New York.

Physical and Chemical Constants and Some Mathematical Functions. G. W. C. Kaye and T. H. Laby. 161 pp. Price, 14s. net. Longmans, Green & Co., London.

Pneumatic Conveying. E. G. Phillips. 103 pp. Price, 2s. 6d. Sir Isaac Pitman & Co., London.

Power Alcohol: Its Production and Utilization. G. W. Monier-Williams. 323 pp. Illustrated. Price, 22s. Oxford University Press, London.

Scientist's Reference Book and Diary for 1922. Price, 3s. 6d. net. Jas. Woolley, Sons & Co., Ltd., Manchester, England.

Sugar: The Manufacture of Cane Sugar. L. Jones and F. I. Scard. 2nd edition, revised. 481 pp. Price, 25s. Duckworth & Co., London.

Tanning: Nachweis, Isolierung, Abbau- und Aufbaustudien auf den Gebiete der Gerbstoffe. K. Freudenberg. **Isolierung, Nachweis, und Abbaustudien auf dem Gebiete der Gerbstoffe.** E. Sieburg. Handbuch der Biologischen Arbeitsmethoden. Edited by E. Abderhalden. Section I. Chemische Methoden. Pt. 10, Vol. II. Pp. 439–584. Price, paper, 78 M. Urban & Schwarzenberg, Vienna.

Technical Records of Explosives Supply 1915–1918. No. 6. Synthetic Phenol and Picric Acid. Price, 15s. net. 97 pp. Illustrated. H. M. Stationery Office, London.

Textile Raw Materials and Their Conversion into Yarns; the Study of the Raw Materials and the Technology of the Spinning Process Julius Zipser. 2nd edition, revised and partly rewritten by D T. Nisbet. 488 pp. Illustrated. Price, $5.00. D. Van Nostrand Co., New York.

Vitamins. H. C. Sherman and S. L. Smith. American Chemical Society Monograph. 270 pp. *Corrected price*, $4.00. The Chemical Catalog Co., Inc., New York City.

NEW JOURNAL

Baking Technology. I. K. Russell, Editor. A Journal of Applied Science in Baking. Published monthly by The American Bakers' Association, and the American Institute of Baking, Chicago, Ill. Price, $5.00 a year.

RECENT JOURNAL ARTICLES

Antimony: The Estimation of Small Quantities of Antimony in Copper and Brass. B. S. Evans. *The Analyst*, Vol. **47** (1922), No. 550, pp. 1–9.

Blast Furnace: Disintegration of Blast Furnace Linings. Paul O. Menke. *The Iron Age*, Vol. **109** (1922), No. 8, pp. 528 29.

Cement: The Application of the Fundamental Knowledge of Portland Cement to Its Manufacture and Use. P. H. Bates. *Journal of the Franklin Institute*, Vol. **193** (1922), No. 3, pp. 278–309.

Chemical Warfare and the Arms Treaty. R. S. McBride. *Chemical and Metallurgical Engineering*, Vol. **26** (1922), No. 8, pp. 351–53.

Coal Gas Manufacture. Jerome J. Morgan. *The Coal Industry*, Vol. **5** (1922), No. 2, pp. 87–91.

Concentration of Liquors by Evaporation. James Holmes. *Chemical Trade Journal and Chemical Engineer*, Vol. **70** (1922), No. 1807, pp. 1–3.

Conveying Machinery in the Chemical Industry. George Frederick Zimmer. *Chemical Age* (London), Vol. **6** (1922), No. 141, pp. 230–33.

Cost Accounting: How to Compute the Cost of Colored Fabrics. H. D. Martin. *Color Trade Journal*, Vol. **10** (1922), No. 2, pp. 70–73.

Electric Precipitation. H. J. Bush. *Journal of the Society of Chemical Industry*, Vol. **41** (1922), No. 3, pp. 21*t*–27*t*.

Electrolytic Solution and Deposition of Copper. T. R. Briggs. *Brass World*, Vol. **18** (1922), No. 2, pp. 45–48.

Engineering Methods Applied to Cost Finding. Robert S. Denham. *Industrial Management*, Vol. **63** (1922), No. 2, pp. 67–73.

Flotation: The Function of Oil in Flotation. Dana W. Leeke and Ralph H. Jarvis. *Mining and Scientific Press*, Vol. **124** (1922), No. 7, pp. 223–26.

Glass: Specifications and Standard Methods for Testing Lime-Flint Glass. Arthur E. Williams. *The Glass Industry*, Vol. **3** (1922), No. 3, pp. 47–50.

Glass: Some Properties of Lime-Magnesia Glasses and Their Commercial Application. Part I. Violet Dimbleby, F. W. Hodkin and W. E. S. Turner. **Part II.** S. English and W. E. S. Turner. *Journal of the Society of Glass Technology*, Vol. **5** (1922), No. 20, pp. 352–60.

Iron: Les Méthodes de Dosage du Carbone dans les Fers, Fontes, et Aciers. A. Travers. *Chimie et Industrie*, Vol. **7** (1922), No. 1, pp. 3–12.

Metals: Grain Growth and Recrystallization in Metals. I. Definitions. II. Experimental Data and General Laws. III. Underlying Causes. Zay Jeffries and R. S. Archer. *Chemical and Metallurgical Engineering*, Vol. **26** (1922), No. 8, pp. 343–45; No. 9, pp. 402–10; No. 10, pp. 449–57.

Metals: Remarks on Fatigue Failure of Metal Parts, Their Cause and Prevention. Horace C. Knerr. *Forging and Heat Treating*, Vol. **8** (1922), No. 1, pp. 40–42.

Open-Hearth Furnace Design. A. D. Williams. *The Iron Age*, Vol. **109** (1922), No. 9, 577–79.

Medicinal Plants: Piante Medicinali e Aromatiche in Sardegna. Efisio Mameli. *Giornale di Chimica Industriale ed Applicata*, Vol. **3** (1921), No. 12, pp. 549–55.

Physico-Chemical Studies of Strong and Weak Flours. II. The Imbibitional Properties of the Glutens from Strong and Weak Flours. Paul Francis Sharp and Ross Aiken Gortner. *Journal of Physical Chemistry*, Vol. **26** (1922), No. 2, pp. 101–36.

Porosity: VI. Determination of Porosity by the Method of Gas Expansion. Edward W. Washburn and Elmer N. Bunting. *Journal of the American Ceramic Society*, Vol. **5** (1922), No. 2, pp. 112–29.

Radioactivity: La Ororadioattivita delle Acque Minerali. R. Nasini and C. Porlezza. *Giornale di Chimica Industriale ed Applicata*, Vol. **3** (1921), No. 12, pp 543–45.

Rosin: Les Progrès Récents dans les Traitement de la Gemme Landaise. Maurice Vèzes and Georges Dupont. *Chimie et Industrie*, Vol. **7** (1922), No. 1, pp. 13–22.

Rubber Mixes and the Question of Accelerators. Joseph L. Rosenbaum.' *The India-Rubber Journal*, Vol **63** (1922), No 6, pp 13–19.

Steel: Theory of the Heat Treatment of Steel. Walter M. Mitchell. *Forging and Heat Treating*, Vol. **8** (1922), No. 1, pp. 52–56; No. 2, pp. 114–18.

Steel: New Etching Method Develops Figures Ascribed to the Influence of Force. Ad. Fry. *Forging and Heat Treating*, Vol. **8** (1922), No. 2, pp. 99–104. Translated from *Stahl und Eisen*.

Sulfuric Acid: La Fabrication de l'Acide Sulfurique par le Procédé de Contact. H. Braidy. *L'Industrie Chimique*, Vol. **8** (1922), No. 97, pp. 46–49.

Synthetic Medicinals: The Manufacture of Synthetic Medicinal Chemicals in America. Alfred S Burdick. *Journal of the American Pharmaceutical Association*, Vol. **11** (1922), No. 2, pp. 98–110.

Tan Liquors: Some Thoughts on the Measurement of the Plumping Value of Tan Liquors. H. C. Reed and T. Blackadder. *Journal of the American Leather Chemists Association*, Vol. **17** (1922), No. 3, pp. 109–15

Tungsten: Fabrication du Tungstène Métallique. Gustave Bessa. *L'Industrie Chimique*, Vol. **9** (1922), No. 96, pp. 2–6.

Water-Proofing Efficiency of Some Bi- and Trivalent Salts of Higher Fatty Acids and Their Adsorption by the Fibers of Paper. Shanti Swarupa Bhatnagar. *Journal of Physical Chemistry*, Vol **26** (1922), No. 1, pp. 61–71.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Compressed-Air Blowers as an Aid to Metal-Mine Ventilation. R. V. Ageton. *Reports of Investigations* **2309.** 6 pp. Issued January 1922.

Fifth Semiannual Motor Gasoline Survey. A. D. Bauer and N. A. C. Smith. *Reports of Investigations* **2328.** 8 pp. Issued February 1922.

Mine Timber Preservation. R. R. Hornor and G. M. Hunt. *Reports of Investigations* **2321.** 19 pp. Issued February 1922.

Monthly Statement of Coal-Mine Fatalities in the United States, November 1921. W. W. Adams. 8 pp. Paper, 5 cents.

Platinum. *Reports of Investigations* **2326.** 6 pp. Issued February 1922.

Properties of Typical Crude Oils from the Producing Fields of Kansas. E. W. Dean, M. B. Cooke and A. D. Bauer. *Reports of Investigations* **2322.** 2 pp. Issued February 1922.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. *Reports of Investigations* **2317.** 39 pp. Issued January 1922.

Some Factors Affecting Products from Destructive Distillation of Oil Shales. L. C. Kerrick. *Reports of Investigations* **2324.** 5 pp. Issued February 1922.

Soapstone. R. B. Ladoo. *Reports of Investigations* **2327.** Issued February 1922. 4 pp.

Subject Lists of Reports of Investigations. (This list covers all reports issued up to December 31, 1921.) *Reports of Investigations* **2316.** 14 pp. Issued January 1922.

Sugar-Tube Method of Determining Rock Dust in Air. A. C. Fieldner, S. H. Katz and E. S. Longfellow. *Technical Paper* **278.** 42 pp. Paper, 10 cents.

Unsaturated Hydrocarbon Constituents of Gas from Destructive Distillation of a Water-Gas Tar and Coal Mixture. R. L. Brown. *Reports of Investigations* **2318.** 6 pp. Issued February 1922.

Water-Gas-Tar Emulsions. W. W. Odell. *Reports of Investigations* **2331.** 5 pp. Issued March 1922.

Bureau of Standards

Manufacture and Properties of Steel Plates Containing Zirconium and Other Elements. G. K. Burgess and R. W. Woodward. *Technologic Paper* **207.** Paper, 20 cents.

Note on the Preparation of Mannose. E. P. Clark. *Scientific Paper* **429.** Paper, 5 cents.

Report of 14th Annual Conference on Weights and Measures. *Miscellaneous Publication* **48.** Paper, 20 cents.

Standard Samples Issued or in Preparation. *Circular* **25** (Supplement). Supersedes supplement issued April 7, 1921. 6 pp.

Congressional Committees

Mr. Ford's Muscle Shoals Proposition. Hearings before the Committee on Military Affairs, House of Representatives.

Part 1—Statement of Hon. John W. Weeks, Secretary of War. February 9, 1922 67 pp.

Part 2—Statement of Gen. C. C. Williams. February 9, 1922. 37 pp.

Part 3—Statement of Maj. Gen. Beach and Col. Hull. February 10, 1922. 92 pp.

Part 4—Statement of Major Burns. February 13, 1922. 35 pp.

Part 5—Statement of William B. Mayo, Chief Engineer of the Ford Motor Company, Detroit, Mich. February 13–14, 1922. 67 pp.

Part 6—Statements of J. W. Taylor, member of Congress from Tennessee; A. A. Taylor, Governor of Tennessee; R. C. Tolman, Director, Fixed Nitrogen Research Laboratory, Department of Agriculture; Milton Whitney, Chief of the Bureau of Soils, Department of Agriculture. February 14–15, 1922. 37 pp.

Part 7—Statement of J. W. Worthington, Chairman, Executive Committee, Tennessee River Improvement Association. February 16–17, 1922. 55 pp.

Part 8—Statement of Hugh L. Cooper, Consulting Engineer, Stamford, Conn. February 17, 1922. 21 pp.

Part 9—Statement of Mr. Swann. February 17, 1922. 11 pp.

Part 10—Statement of Messrs. Hammitt, McDowell, Silver, Bower, Dent, and Martin. February 20, 1922. 261 pp.

Petroleum—Extension of Time on Oil and Gas Permits. Report to accompany H. R. 8344; submitted by Mr. Smoot. S. Rp. 376. 2 pp. January 5, 1922.

Pollution of Navigable Waters, Hearings on Subject of Pollution of Navigable Waters, December 7 and 8, 1921. Part II. 80 pp.

Department of Agriculture

Relation of Initial Temperature to Pressure, Vacuum, and Temperature Changes in the Container during Canning Operations. C. A. Magoon and C. W. Culpepper. *Department Bulletin* **1022.** 51 pp. Paper, 10 cents. Issued February 3, 1922.

Studies in the Clarification of Unfermented Fruit Juices. J. S. Caldwell. *Department Bulletin* **1025.** 30 pp. Issued January 23, 1922.

Geological Survey

Cobalt, Molybdenum, Nickel, Tantalum, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1920. F. L. Hess. Separate from Mineral Resources of the United States, 1920, Part I. 17 pp. Published February 20, 1922

Colemanite in Clark County, Nevada. L. F. Noble. *Bulletin* **735-B.** Separate from Contributions to Economic Geology, 1922, Part I. 17 pp. Published February 23, 1922.

Gold, Silver, Copper, Lead, and Zinc in Arizona in 1920. Mines Report. V. V. Heikes. Separate from Mineral Resources of the United States, 1920, Part I. 26 pp. Published January 19, 1922.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1919. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1919, Part I. 42 pp. Published January 30, 1922.

Salt, Bromine, and Calcium Chloride in 1920. R. W. Stone. Separate from Mineral Resources of the United States, 1920, Part II 9 pp. Published February 21, 1922.

Talc and Soapstone in 1920. Edward Sampson. Separate from Mineral Resources of the United States, 1920, Part II. 13 pp. Published January 20, 1922.

Public Health Service

Contaminated Oysters Source of Typhoid Epidemic at Havre, France. *Public Health Reports*, **37** (February 24, 1922), 422–3.

Notes on the Efficiency of Various Systems of Air-Conditioning in a Munitions Factory. C.-E. A. Winslow and Leonard Greenburg. *Public Health Reports*, **37** (February 10, 1922), 275–91.

The Determination of Hydrogen-Ion Concentration. F. H. McCrudden. *Public Health Reports*, **37** (February 17, 1922), 334–48.

The Treatment of Carbon Monoxide Poisoning. R. R. Sayres and H. R O'Brien. *Public Health Reports*, **37** (February 10, 1922), 271–4.

Tariff Commission

Tariff Information Surveys. Revised edition, 1921–22. FL-28. On articles in Paragraphs 546–560 of Tariff Act of 1913 and related articles in other paragraphs. **Ores of ferro-alloys.** 96 pp. Paper, 10 cents.

MARKET REPORT—MARCH, 1922

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

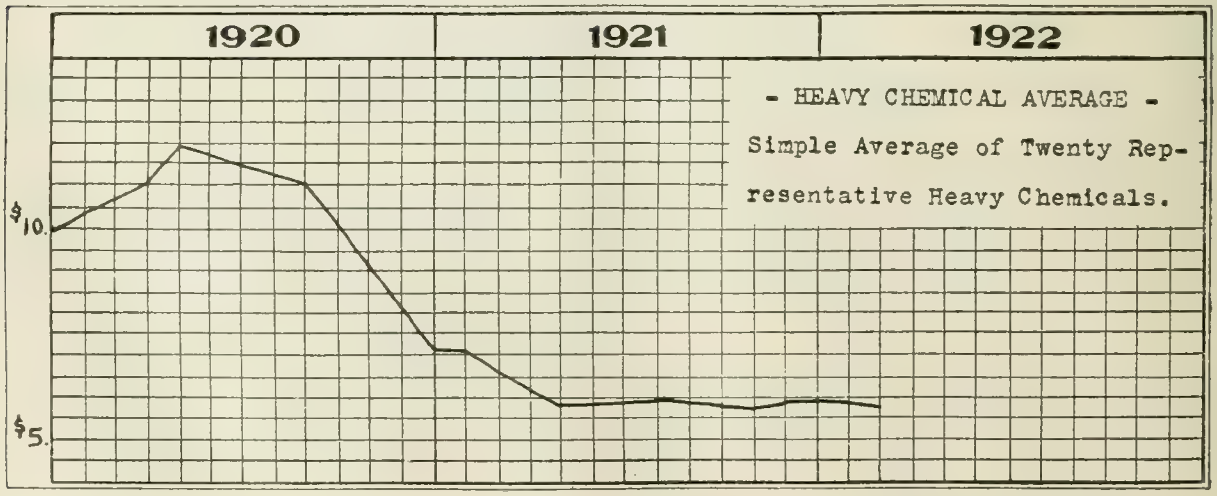
INORGANIC CHEMICALS

		Mar. 1	Mar. 15
Acid, Boric, cryst., bbls	lb.	.12$^3/_4$	.12$^3/_4$
Hydrochloric, com'l, 20°	lb.	.01$^1/_4$	.01$^1/_4$
Hydrofluoric, 30 p. c., bbls.	lb.	.07	.07
Hydriodic, sp. gr. 1.150	oz.	.19	.19
Nitric, 42°	lb.	.06$^3/_4$	.06$^3/_4$
Phosphoric, 50% tech	lb.	.10	.10
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66° tks. wks.	ton	16.00	16.00
Oleum 20%	ton	22.00	22.00
Alum, Ammonia, lump	lb.	.03$^1/_2$	.03$^1/_2$
Potash, lump	lb.	*.03$^1/_4$	*.03
Chrome	lb.	.06$^1/_2$	.06$^1/_2$
Soda, ground	lb.	.03$^1/_2$	.03$^1/_2$
Aluminium Sulfate (iron-free)	lb.	.02$^3/_4$	.02$^3/_4$
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	.07$^1/_2$	.07$^1/_2$
Ammonia, Anhydrous	lb.	.30	.30
Ammonia Water, drums, 26°	lb.	.07$^1/_2$	.07$^1/_2$
Arsenic, white	lb.	.07$^1/_2$	.07$^1/_2$
Barium Chloride	ton	*60.00	*70.00
Nitrate	lb.	*.06$^1/_2$	*.06
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works,	100 lbs.	2.00	1.90
Borax, cryst., bbls	lb.	.05$^1/_2$	.05$^1/_2$
Bromine, pure, wks	lb.	.20	.20
Calcium Chloride, fused, f. o. b. N. Y.	ton	24.75	24.75
Chalk, precipitated, light	lb.	.04	.04
China Clay, imported	ton	18.00	18.00
Chlorine, liquid	lb.	.06	.06
Copper Sulfate	100 lbs.	5.55	5.40
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.05	4.05
Lead Acetate, white crystals	lb.	.11	.11
Nitrate	lb.	.15	.15
Red American	lb.	.08	.08
White American	lb.	.07$^1/_4$	.07$^1/_4$
Lime Acetate	100 lbs.	1.75	1.75
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, tech.	lb.	.06	.06
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*51.00	*49.00
Phosphorus, yellow	lb.	*.25	*.25
Red	lb.	*.25	*.25
Plaster of Paris	bbl.	4.25	4.25
Potassium Bichromate	lb.	.10	.10
Bromide, imported	lb.	*.14	*.17
Carbonate, calc., 80–85%	lb.	.04$^1/_2$	.04$^1/_2$
Chlorate, cryst.	lb.	*.05$^1/_2$	*.05$^1/_2$
Hydroxide, 88–92%	lb.	*.05$^3/_4$	*.06
Iodide, bulk	lb.	3.15	3.15
Potassium (*Concluded*)			
Nitrate	lb.	.08	.08
Permanganate U. S. P.	lb.	*.14	*.14
Prussiate, Red	lb.	.75	.60
Yellow	lb.	.25	.25
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.43	.43$^1/_2$
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	*1.65	*1.65
Caustic, 76%	100 lbs.	*3.30	*3.65
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.30	2.30
Bichromate	lb.	.07$^3/_4$	.07$^3/_4$
Bisulfite, powd	lb.	.04$^1/_2$	.04$^1/_2$
Chlorate	lb.	.07	.07
Cyanide	lb.	.26	.26
Fluoride, technical	lb.	.10	.10
Hyposulfite, bbls	100 lbs.	3.25	3.25
Nitrate, 95%	100 lbs.	2.35	2.85
Nitrite	lb.	.08	.09$^1/_2$
Prussiate, yellow	lb.	.18$^1/_2$	.18$^1/_2$
Phosphate (di-sodium), tech.	lb.	.04	.04
Silicate, 40°	lb.	.01	.01
Sulfide, 60% fused	lb.	*.04$^1/_4$	*.04$^1/_4$
Strontium Nitrate	lb.	*.09	*.09
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride, 50% sol'n	lb.	.10$^1/_4$	.10$^1/_4$
Oxide	lb.	.37	.37
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.08	.08

*Resale or Imported (not an American makers price).

ORGANIC CHEMICALS

		Mar. 1	Mar. 15
Acetanilide, U. S. P. bbls	lb.	.31	.31
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.09	.09
Acetylsalicylic, 100 lbs	lb.	.80	.80
Benzoic, U. S. P., ex-toluene	lb.	.60	.60
Carbolic, cryst., U. S. P., drs.	lb.	.12	.14
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, kegs	lb.	*.44	*.44$^1/_2$
Oxalic, cryst., bbls	lb.	.12	.11$^1/_2$
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.24	.26
Tannic, U. S. P., bbls	lb.	.70	.70
Tartaric, crystals, U. S. P.	lb.	*.24	*.25
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12	.11$^1/_2$
Alcohol, denatured, complete	gal.	.35	.35
Ethyl, 190 proof, bbls	gal.	4.75	4.75
Amyl Acetate	gal.	2.15	2.15



Courtesy of Drug & Chemical Markets

		Mar. 1	Mar. 15
Caffeine Alkaloid	lb.	3.75	3.75
Camphor, Jap, refined, cases	lb.	.93	.88
Carbon Bisulfide	lb.	.06	.06
Tetrachloride	lb.	.10$^{1}/_{2}$	.10
Chloroform, U. S. P., drums	lb.	.37	.37
Creosote, U. S. P.	lb.	.40	.40
Cresol, U. S. P.	lb.	.12	.12
Dextrin, corn	100 lbs.	2.79	2.89
Imported Potato	lb.	.08$^{1}/_{2}$	.08$^{1}/_{2}$
Ether, U. S. P., conc., 100 lbs.	lb.	.14	.14
Formaldehyde, bbls	lb.	.09	.08$^{1}/_{2}$
Glycerol, dynamite, drums	lb.	.14	.14
Methanol, pure, bbls	gal.	.75	.75
Methylene Blue, Med	lb.	4.00	4.00
Petrolatum, snow-white	lb.	.13	.12$^{1}/_{2}$
Light Amber	lb.	.05	.04$^{1}/_{2}$
Green	lb.	.03	.02$^{3}/_{4}$
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	2.22	2.32
Potato, Jap	lb.	.06$^{1}/_{2}$	.06$^{1}/_{2}$
Rice	lb.	.18	.18
Sago	lb.	.04	.04

OILS, WAXES, ETC.

		Mar. 1	Mar. 15
Beeswax, pure, white	lb.	.33	.33
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10$^{1}/_{2}$	.10
Ceresin, yellow	lb.	.08	.08
Corn Oil, crude, tanks, mills	lb.	.08	.10
Cottonseed Oil, crude, f. o. b. mill	lb.	.10	.09$^{3}/_{4}$
Linseed Oil, raw (car lots)	gal.	.86	.84
Menhaden Oil, crude (southern)	gal.	.42	.40
Neat's-foot Oil, 20°	gal.	1.32	1.32
Paraffin, 128–130 m. p., ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs	bbl.	5.35	5.35
Rosin Oil, first run	gal.	.36	.36
Shellac, T. N.	lb.	.72	.76
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.69	1.69
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.77	.77
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.88	.86

METALS

		Mar. 1	Mar. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.35	4.35
Bismuth	lb.	2.10	2.20
Copper, electrolytic	lb.	.12$^{3}/_{4}$	.13
Lake	lb.	.12$^{3}/_{4}$	.13
Lead, N. Y.	lb.	.04$^{3}/_{4}$	.04$^{3}/_{4}$
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	90.00	90.00
Quicksilver, flask	75 lbs. ea.	51.00	49.00
Silver, foreign	oz.	.63$^{3}/_{4}$	.63$^{3}/_{8}$
Tin	lb.	.30$^{3}/_{4}$	.28$^{3}/_{4}$
Tungsten Wolframite	per unit	2.00	2.00
Zinc, N. Y.	100 lbs.	4.82$^{1}/_{2}$	4.95

FERTILIZER MATERIALS

		Mar. 1	Mar. 15
Ammonium Sulfate, export	100 lbs.	2.60	3.10
Blood, dried, f. o. b. N. Y.	unit	3.75	4.00
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works	unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.60	.60
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.25 & .10	3.25 & .10

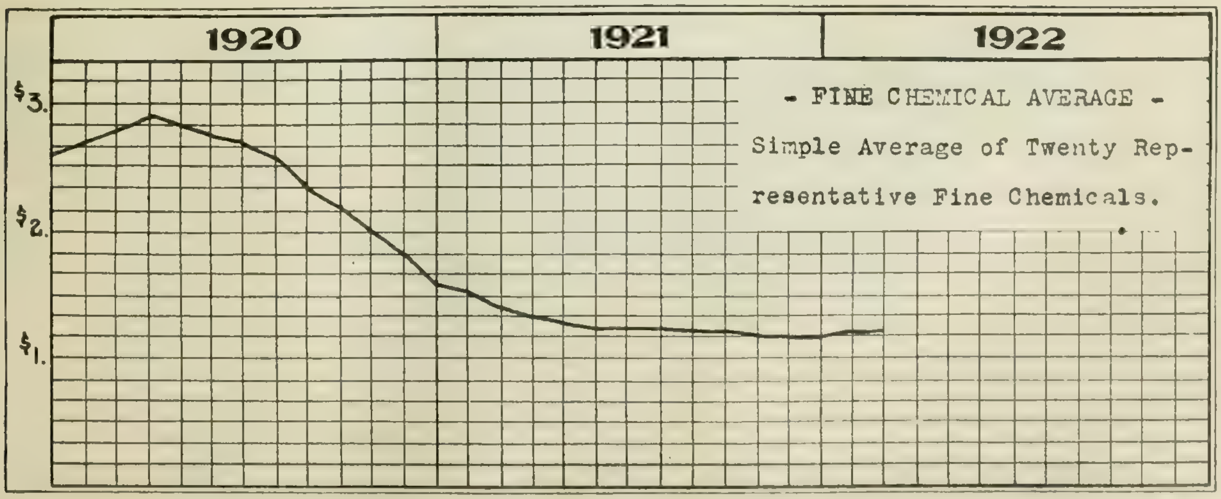
COAL-TAR CHEMICALS

Crudes

		Mar. 1	Mar. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure, tanks	gal.	.29	.29
Cresol, U. S. P.	lb.	.12	.12
Cresylic Acid, 97–99%	gal.	.50	.50
Naphthalene, flake	lb.	.07$^{1}/_{2}$	.07$^{1}/_{2}$
Phenol, drums	lb.	.12	.12
Toluene, pure, tanks	gal.	.30	.30
Xylene, 2 deg. dist. range, tanks	gal.	.45	.45

Intermediates

		Mar. 1	Mar. 15
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.00	2.00
H	lb.	.85	.85
Metanilic	lb.	1.00	1.00
Monosulfonic F	lb.	2.30	2.30
Naphthionic, crude	lb.	.65	.65
Nevile & Winther's	lb.	1.30	1.25
Phthalic	lb.	.32	.32
Picric	lb.	.20	.20
Sulfanilic	lb.	.24	.24
Tobias'	lb.	1.60	1.50
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.16	.16
Aniline Salt	lb.	.24	.24
Anthraquinone	lb.	1.40	1.40
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.55	.55
U. S. P.	lb.	1.40	1.40
Benzidine (base)	lb.	.90	.85
Benzidine Sulfate	lb.	.70	.85
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75



Courtesy of Drug & Chemical Markets

		Mar. 1	Mar. 15
p-Dichlorobenzene	lb.	.17	.17
Diethylaniline	lb.	60	60
Dimethylaniline	lb.	38	38
Dinitrobenzene	lb.	21	21
Dinitrotoluene	lb.	25	.25
Diphenylamine	lb.	60	.60
G Salt	lb	7	.70
Hydroquinol	lb	1.35	1 35
Metol (Rhodol)	lb	3.50	3.50
Monochlorobenzene	lb	.10	.10
Monoethylaniline	lb	1.00	1.00
a-Naphthylamine	lb	.30	.30
b-Naphthylamine (Sublimed)	lb	1.50	1.50
b-Naphthol, dist	lb	.28	.28
m-Nitroaniline	lb	.80	.77
p-Nitroaniline	lb	.77	.77
Nitrobenzene, crude	lb	.10	.10
Rectified (Oil Mirbane)	lb	.10	.10
p-Nitrophenol	lb	.75	.75
p-Nitrosodimethylaniline	lb	—	—
o-Nitrotoluene	lb	.15	.15
p-Nitrotoluene	lb	.70	.70
m-Phenylenediamine	lb	1.05	1.05
p-Phenylenediamine	lb	1.50	1 50
Phthalic Anhydride	lb.	.35	.35
Primuline (Base)	lb.	2.00	2.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb	1.75	1.75
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.35	.35
Tolidine (Base)	lb.	1.20	1.20
Toluidine, mixed	lb.	.30	.30
o-Toluidine	lb.	.20	.20
p-Toluidine	lb.	1.00	1.00
m-Toluylenediamine	lb.	1.05	1.05
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Mar. 1	Mar. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50
Fuchsin	lb	2.00	2.00
Orange III	lb	.50	.50
Red	lb.	.85	.85
Alkali Blue, domestic	lb	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	6.00	6.00
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Mar. 1	Mar. 15
Black	lb.	.55	55
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	2 00	2.00
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	1.10	1.10
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	1.75	1 75

Oil Colors

		Mar. 1	Mar. 15
Black	lb	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb	.90	.90

Sulfur Colors

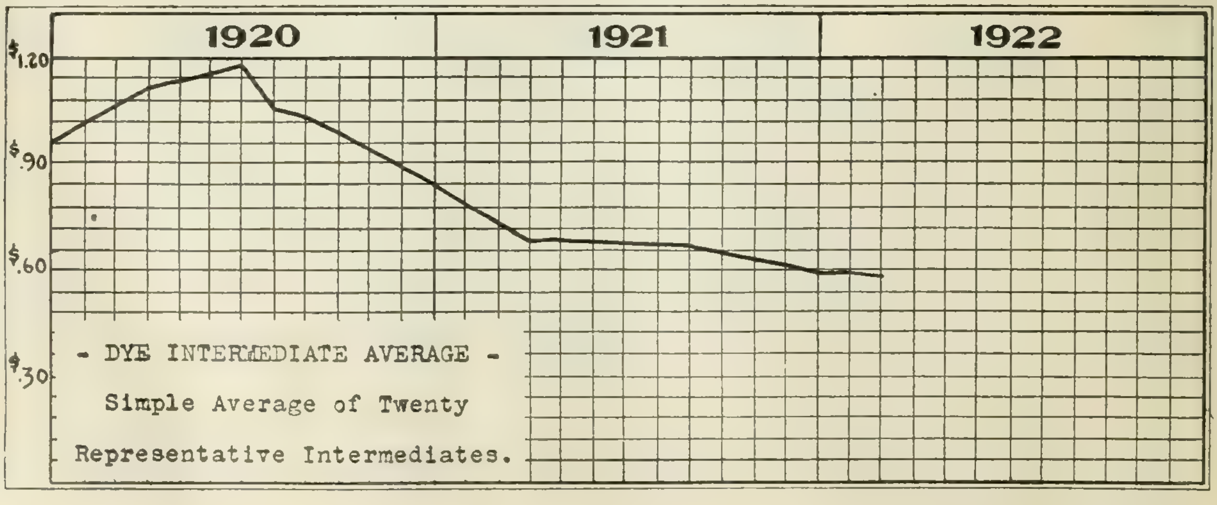
		Mar. 1	Mar. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.60	.60
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.75	.75

Chrome Colors

		Mar. 1	Mar. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb	.85	.85
Chrome Black, domestic	lb.	.55	.55
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Mar. 1	Mar. 15
Auramine, O, domestic	lb.	2.00	2.00
Auramine, OO	lb.	2.50	2.50
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	2.25	2.25
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	1.60	1.60
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc	lb.	8.00	8.00
Victoria Blue, base, domestic	lb.	3.50	3.50
Victoria Green	lb.	1.50	1.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00



Courtesy of Drug & Chemical Markets

The Journal of INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society

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Volume 14 MAY 1, 1922 No. 5

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Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, $1.00, Canada, Cuba and Mexico excepted.
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.
Member of Audit Bureau of Circulations

EDITORIALS

Importation and an Opportunity

We have frequently been asked what are the present conditions under which apparatus and chemicals can be imported. To supply the answer we have made a careful investigation, and believe the results justify editorial comment.

It seems inadvisable to undertake importation of miscellaneous lists at the present time. Where highly specialized pieces of apparatus are required and the purchaser is prepared to take any and all risks involved, including annoying delays, there is, of course, more reason for importation than where miscellaneous lists for students are to be purchased at definite prices and for delivery at a specified time. We find that with the present German governmental control of glassware prices through export regulations, there is little, if any, price advantage in importing glassware, porcelain, etc., from that country. The time of delivery is most uncertain, while quality is often inferior to that of pre-war years. This matter of quality and workmanship applies both to apparatus and to chemicals. Much inferior apparatus has come in unmarked and is called American in case of complaint. One of the best known makes of reagents shows almost unbelievable deterioration as judged by recent lots, and we are informed that the actual management of the works has recently fallen into new hands. There is therefore little, if any, advantage in price, quality, or delivery. Last year one of our best known supply houses purchased only 6 per cent of its stock from Germany, despite the great advantage in exchange.

The present unsatisfactory condition under which importations can be made presents a wonderful opportunity to American manufacturers and to our dealers. There is also a need for constructive work on the part of the users. Let us treat these points in turn.

We need not rehearse the wonderful achievements of our manufacturers thus far. American manufacturers have made good in glass, in porcelain, in pyrometers, in hemacytometers, in electrical measurement apparatus, analytical balances, electric furnaces, electric ovens, all sheet-metal ware, all hardware, and a long list of devices which call for just as much ingenuity, resourcefulness, and persistence for their development as is the case with any chemical apparatus. Now is the time for American manufacturers to win all of the American and a share of the world market in face of foreign competition by the simple method of making the best apparatus at equal or lower prices if this is possible, but always the best. Many doubt whether the American market can ever be secured by American makers on a price basis. There are too many handicaps. Quality must be made the distinction. Americans cannot be expected to pay high prices for inferior material, but they soon learn the real economy of buying goods of quality. A large stock of a foreign glass lies unsalable in New York because even students have learned that in the long run an American glass is not only better but more economical.

In going about, we have heard of instances where manufacturers have not been willing to coöperate fully with users in providing glassware and other items in accordance with reasonable specifications. Manufacturers must go a little more than half way if the best results for all concerned are to be obtained.

The dealers have their opportunity in helping to place the purchase of large quantities on a really sound basis. Has the time not come when the man who buys an original package of apparatus or chemicals should have the lowest price for that package, regardless of the rest of his order? Why should a laboratory be given special consideration because of the size of a miscellaneous order over another laboratory which is willing to buy in standard packages? To the best of our knowledge, this condition does not obtain in other lines of business. The grocer who buys a barrel of sugar gets the lowest price on the barrel without regard to the number of boxes of raisins, prunes, and soap which accompany the order. Each item is priced on the quantity of that item.

Some dealers have also been somewhat responsible for present methods of buying by encouraging large laboratories to estimate in March what they will need in October. The result has been that many an institution has found itself with quantities of material lying idle in the stockroom, has bought unwisely except for a few standard items, and has in many cases practiced false economy. It would be an excellent thing for all concerned if the dealers would agree upon a sound business sales policy and seek coöperation of the large buyers in following out that policy.

It devolves upon the consumer to determine what is quality. For example, rubber manufacturers have come to know that many orders for tubing and stoppers are placed solely on the basis of price, and the maker finding the best way for introducing a high percentage of various fillers and substitutes gets the business. The result is that the best apparatus dealers can no longer depend upon regular stock production for laboratory use, but are compelled to have special tubing and stoppers made to insure uniformity and reasonable quality for the purpose intended.

And so with many other items in the list of 15,000 which make up the modern chemical apparatus catalog. Our Committee on Guaranteed Reagents and Standard Apparatus is doing constructive work of value. Might not that Committee or some other be charged with the duty of determining standards of quality as a protection to the purchaser and also to the faithful manufacturer and dealer who endeavors to give quality at a reasonable price?

The whole situation is after all an economic one. We have stated some of the factors involved. We can accomplish the best for all concerned if we can agree upon a working program. What is your experience?

The Freight Factor

Our chemical industry has been confronted with one handicap after another and has already overcome difficulties greater than those ever presented to other commercial enterprises. Among the difficulties which are common to industry in general, but which affect chemistry to an unusual degree, the freight factor is an example.

Other countries do not meet this difficulty. They are smaller, have consuming markets near production centers, or have the advantage of waterways like the Rhine. The sea enables many producers to deliver goods at a rate which practically stifles the corresponding American industry. Thus, grades of clay for certain porcelain insulators are brought from Wales at ten shillings per ton freight, while the same grades from American pits carry a freight of from nine to ten dollars a ton to consuming markets. One of the chief handicaps in selling American potash in the eastern consuming market is the freight item, which accounts for more of the difference in price between American and imported potash salts than the proposed tariff would compensate.

All industry goes back to power, and to-day the freight on some grades of coal is more than the same kinds of coal cost, delivered in factory bunkers, a few years ago. It is fairly well agreed that much of our freight cost is due to the fuel item and to wages paid railroad labor in excess of those paid the same class of labor in other industries. In the case of railroad labor, statistics will be helpful. The following figures are based upon data compiled by the Illinois Manufacturers Association:

There are approximately 380,000 employees who are directly concerned with train operations, and 1,341,000 workers who have nothing directly to do with trains. The latter are the shop craft labor, whose wages comprise nearly 80 per cent of the railway payroll. They are about 25 per cent overpaid, as compared with other industries. The figures show the following details:

	NUMBER	Average per Hour Quarter to June 30, 1921	Per Year 1920
Machinists	66,127	$ .883	$2,234
Boiler makers	20,867	.893	2,314
Masons and bricklayers	1,210	.734	1,750
Blacksmiths	10,997	.874	2,119
Structural iron workers	715	.801	2,037
Carpenters	52,459	.758	1,808
Painters and upholsterers	13,201	.813	1,859
Electricians	15,247	(per day) 7.072	2,215
Airbrake men	8,194	.845	2,141
Car inspectors	26,923	.847	2,313
Car repairers	90,127	.819	1,997
Other skilled laborers	60,526	.829	2,087
Mechanics helpers and apprentices	139,298	.628	1,548
TOTAL SHOPMEN	505,891		
Section men	276,829	.451	1,179
Enginehouse men	76,993	.54	1,527
Other unskilled laborers	121,197	.520	1,306
TOTAL	980,910		
Clerks	243,965	.701	1,647
Station service	116,968	.546	1,373
GRAND TOTAL	1,341,843		
Trainmen			
YARD EMPLOYEES			
Engineers	23,747	.93	2,650
Firemen	23,923	.73	2,005
Conductors	23,513	.89	2,514
Brakemen	58,548	.83	2,265
Switch tenders	6,779	.64	1,795
Others	5,088	.54	1,436
ROAD TRAINMEN			
Freight engineers	35,717	1.154	3,436
Firemen	38,590	.875	2,452
Conductors	29,027	.977	3,008
Brakemen	72,203	.776	2,331
Passenger engineers	13,190	1.369	3,326
Passenger firemen	12,724	1.053	2,475
Passenger conductors	11,070	1.148	2,971
Passenger baggagemen	5,899	.863	2,240
Passenger brake and flagmen	16,291	.847	2,094
Others	3,711	.663	1,775
Total	380,120		
Hostlers	12,439		
GRAND TOTAL	392,120		

These figures show that the so-called common skilled labor such as is employed in the repairing of freight cars receives an average of 84 cents an hour, while the prevailing rate in the manufacturing industry is about 45 cents an hour. No one can object to the wages paid those who have in their care not only such expensive equipment as locomotives but the safety of many lives, but it does seem unnecessary to burden business in general by the payment to other classes of labor of such wages as these statistics show. Many an instructor in our educational institutions and no small percentage of professional men look upon these annual earnings with a little wistfulness. It seems unlikely that transportation costs can be brought back to normal unless some adjustments can be made in the wages of some classes of railroad labor. When this is done the chemical industry will be encouraged, along with other manufacturers.

The Tariff Bill

The following extract is taken from the Report to accompany the tariff bill (H. R. 7456), which was submitted to the Senate by the Chairman of the Finance Committee on April 11, 1922.

DYES AND SYNTHETIC ORGANIC CHEMICALS

It was found that the rates provided for dyes and coal-tar chemicals, after the limited embargo provisions covering these products had been eliminated on the floor of the House of Representatives, were wholly inadequate to protect the domestic industry.

It is common knowledge that Germany had a monopoly of the world's trade in dyes prior to the war. Although our domestic industry has made great strides during and since the war, when these products have been admitted to the United States only under license, as provided by the emergency tariff act of May 27, 1921, and although our industry is capable of supplying between 85 and 90 per cent of the quantity required of domestic consumers, it has not attained a point in efficiency of manufacture where it can hope to compete with the well-organized industry which exists in Germany. Your Committee has reached the conclusion that no rates in American tariff history would be adequate to protect this industry.

Your Committee therefore recommends that the provisions of the emergency tariff act relating to dyes and synthetic organic chemicals be extended for a period of one year after the tariff bill becomes a law. In subdivision (*d*) of Section 315 the President is also authorized, if upon investigation he ascertains that the rates specified upon coal-tar intermediates and dyes do not equalize the differences in competition here and abroad, or if he ascertains that an industry in the United States is being or is likely to be injured by reason of the importation of like intermediates or dyes into the United States, to issue a proclamation stating such fact and to continue the dye and chemical control act in force for a further period not to exceed one year. In addition, the following rates of duty on these products are proposed: 50 per cent plus 7 cents per pound on intermediates and 60 per cent plus 7 cents per pound on finished coal-tar products. Under the administrative provisions of the bill, the President has been given authority to base these rates on American values of similar competitive articles and also to increase or decrease the rates not exceeding 50 per cent, if, after investigation, he may find such action necessary. The extension of the dye control provisions of the emergency tariff act for one year (and two years if necessary) will give the President sufficient time to investigate conditions in the domestic dye and coal-tar industry, to ascertain what products can be protected by the rates specified in this bill, to determine the products on which it will be necessary to assess duties based upon American valuation, and to decide what increase in rates will be necessary in order that all branches of this industry may become firmly established in the United States.

It will take courage to go forward with development on a large scale under this bill. A great gain has been made, however, in the matter of time. This can be used to advantage in making sure that a larger proportion of Congress becomes familiar with the conditions involved.

Technical Information Service

Organizations of business men are wont to establish a variety of services designed to the profit of the members of the group—legal, taxation, insurance, accounting, banking, and freight are subjects usually receiving special consideration. But it has remained for the Associated Industries of Massachusetts to establish a technical information service for its members. This is a forward step of direct interest to chemists and establishes a precedent which should assist chemists in other localities in bringing home to manufacturers a realization that in applied science they have a reliable anchor to windward.

New England has been a favorable place for such activities because of its relatively small area, the concentration of its diversified manufacturing, and the agencies at work. The several colleges and universities and technical schools have been active centers, aided by several commercial laboratories. When one chemist does a really good piece of work, all chemists and the science are directly benefited. If the work is poor, all suffer. We quote from the Association's announcement:

> The service is equipped to answer inquiries on the fundamental processes employed in manufacturing operations, such as steam generation, water softening, lubrication, heating, drying of materials, filtration, distillation, evaporation, dyeing, etc., and to supply members with knowledge which will be of material aid in solving problems of construction, the properties of building materials, the selection of the more important types of equipment for certain operations, the erection of machinery, and the like. It is also in a position to direct members to sources of information on technical subjects and to places where materials or equipment can be obtained to the best advantage.

This is an encouraging sign which should be brought to the attention of business organizations everywhere.

Is a Commercial War between Chemists and Business Men Coming?

The United States to-day abounds in chemical knowledge. If the business men do not utilize it properly, the chemists themselves will.

Chemical advice, dearly purchased and highly praised during the war, is now being shelved and disregarded. Perhaps it is only a coincidence that at the same time trade is stagnant, and our hold on foreign markets dwindling.

Hundreds of chemists, vainly looking for positions, will probably be forced to engage in business for themselves. Thus fate may push them into good fortune, and the skeptical business men out of it.

All further talk about the good that chemists can do for manufacturers is wasted. A baker, refusing to take advantage of chemical knowledge, may some day wake up to find that a chemist has opened a bakery shop on the other side of the street. It may easily happen that he will be convinced and bankrupted at the same time.

Chemical knowledge, like many other desirable goods, will not be bought by the public unless it is sold to them. Triumphant competition may eventually be the slogan of a successful although painful selling campaign.

The kind of goods that sells on merit only, without selling effort, is yet to be found. Chemists have relied entirely on the merit of their goods, and have not sold them; manufacturers have refused to believe that anything not advertised on billboards can have merit. As a result, both sides have suffered severely.

Chemists, inclusive of college teachers, need to learn that even an all-wool suit will not sell if a dealer puts it into a dark basement.

Most chemists spend their lives advising manufacturers how to make money. Napoleon was an adviser to two helpless generals at the siege of Toulon, and, while he kept on advising, Toulon held out. One day, Paris instructed Napoleon to take charge, whereupon he carried out his own advices and Toulon fell.

If chemists have as much faith in their advice as they claim they have, they will stop fretting and fuming about the incompetence of business men; they will start to compete with the business men and show them how.

The business men may have to worry about this, but the public will not. They will get their goods better, cheaper, and more uniform than ever before.

Otto Eisenschiml

Distribution of Chemists

Data compiled by the Association of Harvard Chemists throw light upon the distribution of a typical group of men who have concentrated in chemistry while at that institution. The data are based upon letters sent to 950 men, of whom 628 replied. An analysis of the returns shows that 157 of these men are teaching in various colleges, three having reached the grade of president; 38 are teaching in high schools; 40 are graduate students in chemistry; 35 have become physicians and surgeons; 43 are in the employ of the Government; 103 are executives in commercial chemistry; 159 are commercial chemists; and 41 in purely commercial work. In the latter class we find 15 in accounting and finance, 4 in manufacturing and sales other than chemistry, 5 editors and publishers, 9 patent attorneys, and 1 governor of state. Classification of executives in commercial chemistry is as follows: 15 presidents, 10 vice presidents, 4 secretaries, 5 treasurers, 23 managers, 23 superintendents, 8 assistant superintendents, 2 chemical foremen, 3 purchasing agents, 8 sales managers, and 2 salesmen.

Among other things, the above figures indicate the diversity of work which a chemical training makes possible. We believe that if similar figures were available for men who specialized in other sciences, it would be found that chemistry is in an enviable position.

The Earning Power of Research

Aside from chemical control in making the very dense and brilliant lead glass blanks used in making cut glass, chemistry formerly had little to do with producing the finished product. All operations were mechanical. Patterns were marked out on the blank, and steel wheels, with mitered edges and armed with trickling sand and water, were used to make the deep cuts and the finer tracery. Stone wheels next smoothed the roughly cut surfaces. Wooden wheels with pumice and water gave an approach to a polish, and finally rapidly revolving brushes with putty powder (tin oxide) gave the high finish. The men who operated these four types of apparatus were all highly skilled and highly paid. About 1895 attempts were made to utilize the action of hydrofluoric acid on glass, in order to eliminate the two final processes almost entirely. Many difficulties were encountered by the chemists who attempted to control this reaction. Finally, however, they were overcome, and one or two men can now polish the output of a large factory, permitting the laying off of perhaps forty highly paid workers and the selling to the public of fine cut glass ware at much less than it could otherwise be marketed.

As in all such cases the advance is hard, for the time being, on the men laid off, but they eventually do something else for the world, and society in general benefits from the advance.

Frank B. Wade

When Muscle Shoals is leased, it will be in order to make an all-American fertilizer. Phosphoric acid by electric furnace methods from supplies of phosphate rock near at hand suggests itself. American potash is seeking a market. Nitrates will be made on the spot. Such a scheme for a concentrated complete fertilizer sounds feasible, and an all-American fertilizer surely has advertising possibilities.

BIRMINGHAM MEETING AMERICAN CHEMICAL SOCIETY

An unusual opportunity to meet fellow chemists and discuss problems of mutual interest, interested discussion of good papers, and a really uncommon industrial excursion—these were the outstanding points of our spring meeting. The attendance, while less than 400, was made up of representatives from 35 states, from Canada, and one visitor from the far-away isle of Mauritius. The geographical distribution of those in attendance showed the following at the top of the list in the order mentioned:

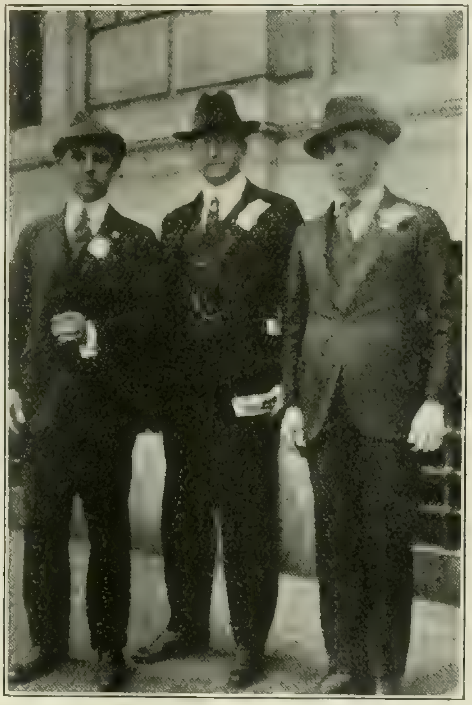
Alabama	51
New York	33
Illinois	32
Ohio	31
District of Columbia	29
Pennsylvania	26

The Local Committee, though laboring under a number of handicaps, did everything possible to make the meeting an unqualified success, and Chairman J. F. Carle with his immediate staff of assistants earned our sincere thanks. The Alabama Technical Association were our hosts at the smoker, while the Tennessee Coal, Iron and Railroad Company contributed to our profit and pleasure to a very great degree.

The SOCIETY was really complimented when the First Methodist Church after due consideration made available their Sunday school rooms for the Division and Section meetings. So far as we know it is the first occasion upon which a church has been used for such meetings of our SOCIETY, and it was the first occasion upon which meetings of a non-religious character had been permitted in this edifice. The balance was swung in our favor by the fact that the church authorities recognize the efforts of chemists to ascertain the truth.

The short distance between the hotel headquarters and meeting places, together with the time allotted upon the program, gave us an unusual opportunity to meet the men and to have time to talk things out. There is no question that chemistry in the South was greatly stimulated by the meeting. The press was generous in its notices of our activities, and because of our visit it will be possible for the achievements of chemistry to be kept before the people by the efforts of the press and those chemists who are willing to tell of their work. The meeting also served to call popular attention to the efforts of chemists who are combining business ability with technical knowledge in the utilization of southern resources.

The excursion upon the 7th deserves particular mention. It might even be called a symposium upon iron and steel. In one day we were shown the mines and quarries necessary for the support of blast furnace and steel mills, the furnaces, the rolling mills turning out their various types of steel products, mills for fabricating steel, the production of wire, nails, fencing, etc.



SOME MEMBERS OF THE LOCAL COMMITTEE
MAX KUNIANSKY, J. F CARLE, J. T. MACKENZIE

In the hope that those expecting to attend the autumn meeting may read these lines, we would emphasize the importance of those traveling by rail to the meetings obtaining certificates when tickets are purchased and bringing these tickets for certification to the meeting. This should be done without regard to whether the purchaser expects to return by the same route or not. Those traveling to Birmingham probably lost $3000 because there were insufficient certificates to entitle the holders to half fare on the return. Had all those who attended from a distance presented certificates, this substantial saving could have been made.

At the General Meeting, following the warm words of welcome from Lieut. Gov. Miller and the representative of the City Commissioners, Dr. Ellwood Hendrick read a tribute to the work of Dr. Baskerville, and Dr. W. A. Noyes presented a statement concerning the work of the late Ciamician. He also paid tribute to the work of von Baeyer and Emil Fischer, obituaries of whom are to appear in the *Journal* of the SOCIETY.

Before opening the scientific part of the morning's program, President Smith referred briefly to the activities of the Local Sections which have most impressed him on his visits during the past year. The coöperation of the Rochester Section with the city Chamber of Commerce, in such economic welfare work as procuring pure pasteurized milk for the city and exterminating rats and other dangerous pests, is only one example of what this active Section is doing in bringing before the public the value of this most essential science. The monthly publications of the Sections, he said, are an index of those who conduct these enterprises. For example, the *Bulletin* of the Chicago Section is breezy, and also homey, and holds out the welcome hand. There is a decidedly wholesome, earnest, scientific atmosphere. He urged a broad knowledge of chemistry. "The more we know of it in its strange and marvelous appearances the better for us. It may be analytical, agricultural, organic, physical, electro, etc., but it is *chemistry*, and the broader our training and equipment the more readily will we be able to follow it in its many varieties. Let us 'prove all things and hold fast to the good.' Let us be *chemists*, with contempt for no one of the forms it may assume in the hands and under the guidance of minds of honest, broadly trained devotees of the science."

Once more it has been demonstrated that meetings of the SOCIETY can be held with great success at some distance from the center of population or where the Section is not large, but where encouragement to local members of the SOCIETY and the advancement of our profession in the locality fully repay the effort involved.

The Council Meeting

About 80 men gathered for the Council Meeting on the evening of April 3 at the Southern Club. In his introductory remarks, made in his well-known happy style, Dr. Smith called attention to the slight regard given the technical experts at the recent conference for the limitation of armament, and noted the present status of the dye embargo. The Secretary then presented a letter from the Chemical Foundation, which was received with profound thanks from the Council on behalf of the SOCIETY. The letter follows:

> FEBRUARY 27, 1922
>
> Dr. Charles L. Parsons,
> Secretary of the American Chemical Society,
> Mills Building, Washington, D. C.
>
> DEAR DR. PARSONS:
>
> I have read your letter of January 10 and sincerely regret that the AMERICAN CHEMICAL SOCIETY, because of lack of funds, has been compelled to stop the publication of the Formula Index and to cut down considerably in the publication of scientific and industrial chemical literature. This retrenchment will be a real blow to the advancement of chemistry in this country, because chemical progress is fundamental to the health and industrial development of the country.
>
> In order that the work of the AMERICAN CHEMICAL SOCIETY may continue without interruption, the Chemical Foundation will supply the money needed to print the Formula Index and to cover the retrenchment which the Directors thought necessary up to $25,000 for the year 1922.
>
> Very truly yours,
> FRANCIS P. GARVAN

In this connection attention was particularly called to the importance of increasing the membership of the SOCIETY. While recognizing that chemists have had the same embarrassments as other folks during the last year or so, it is nevertheless true that from the number who are interested in chemistry in this country it ought to be possible for us to draw a sufficient membership to make it unnecessary to seek support from other sources for our activities. There is no question that industry shows a trend for the better, and chemists should watch their opportunity to gain additional members for the SOCIETY.

President Smith then presented the report of the Priestley Fund Committee, details of which appear on p. 458. A letter from the Patent Commissioner thanking the SOCIETY for its efforts in forwarding the work of the Patent Office was presented, and then came the welcome news that the first two monographs published for the SOCIETY by the Chemical Catalog Company had not only paid their way but had earned certain dividends for the SOCIETY. There is reason to believe that the entire series will be very successful from all viewpoints. A resolution was adopted that publishers of chemical books be asked in the future to indicate the date when books are written or revised, citing these same dates in announcements concerning the volumes. It is obvious that the printing date is of far less importance to scientific men than the date when the copy was actually prepared. The resolution will be brought to the attention of the publishers.

The Cellulose and Petroleum Sections, having asked to be made Divisions, were advised that when by-laws to be presented at the Pittsburgh Meeting had been approved, they would be advanced to the status of Divisions. The Council then voted that in the future Sections would be required to go through a probation period of three years to demonstrate the justification for their formation and the likelihood of their being able to continue in active work before they would be recognized as Divisions. The request for the formation of Local Sections in Hawaii and at Sacramento were granted. The Morgantown, W. Va., request was approved, subject to waivers being given by the Pittsburgh Section and to a possible change in name to avoid future complications. After extended discussion as to whether or not the SOCIETY favored the formation of Local Sections in foreign countries it was decided that no change should be made for the present.

The invitation from the New Haven Section for the spring meeting of 1923 was accepted by unanimous vote. The invitation of San Francisco for late July or early August 1923 was then presented, and the advantages of California were rehearsed in a unique manner by Dr. E. C. Franklin, who told of a few things which are not to be found in California, the claims of enthusiasts to the contrary notwithstanding. Professor R. E. Swain, who had come from the coast for the meeting, urged the acceptance of the invitation when the time comes for the vote. The possibility of our being invited to Ithaca upon the completion of the new laboratory in 1923 was also announced, and President Smith put on record the invitation of Philadelphia for the autumn of 1926, that being the fiftieth anniversary of the formation of the SOCIETY and the time of the sesquicentennial exposition to be held at Philadelphia. Prof. William McPherson was elected a member of the Advisory Committee to succeed H. E. Howe. Prof. Henry Clay White of the University of Georgia, Athens, Ga., was felicitated for his fifty years' continuous service in the department of chemistry at that university.

The Council passed a resolution that at each semiannual meeting of the SOCIETY announcement should be made of the names of donors who had made grants for the promotion of research in chemistry, not only in recognition of their generosity but for the purpose of calling the attention of others to the desire for such grants in an ever-widening field. A motion to instruct the Directors as to the activities which should be restricted in case the budget exceeds the expected income was laid on the table. The status of student members was then discussed, several feeling that because of the increased costs of printing to the SOCIETY, the dues of student members ought to be advanced in conformity with advances made in the dues of the SOCIETY. It was decided, however, to make no change at this time.

Authority was granted to delete the words "the journal of" from the name of the *Journal of Industrial and Engineering Chemistry*, so that beginning with the January 1923 number this journal will be known as *Industrial and Engineering Chemistry*. The President was authorized to appoint a committee of seven to consider a number of suggestions that have been made relative to the activities of the SOCIETY and its various officers and committees. Some have suggested that perhaps our Directors should be elected from specified regions; that a change should be made in the method of electing members of the SOCIETY; that a group of fellows of the SOCIETY should be created, to be elected by the Council for meritorious work in chemistry. These and other suggestions will be considered by the committee which will endeavor to report at the Pittsburgh Meeting. The Council then voted to reaffirm its former decision with respect to intersectional meetings, encouraging these meetings wherever it may be possible to hold them, particularly for the benefit of the younger men who find it inconvenient to attend the spring and fall meetings of the SOCIETY and who deserve an opportunity to present their papers before larger groups than their Section meetings.

The final discussion of the Council had to do with our employment problem. (Report is printed in full on p. 456.) By a very close vote the Council went on record as favoring the establishment of an employment agency which would be especially interested in the chemist, but by an overwhelming vote thought this activity should not be under the auspices of the AMERICAN CHEMICAL SOCIETY. A committee was authorized to confer with other professional men who are now working upon this same question. There were many who felt that the university and the Local Sections have in the employment question an unusual opportunity for service to their chemists. In addition to these activities the need for a central clearing house and coördinating agency was expressed.

The Flower and the Organic Chemist: Perfumes—Natural and Synthetic

By **Marston Taylor Bogert**

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De gustibus non disputandum est is nowhere more clearly applicable than in the field of perfumes. "One man's spinach is another man's poison ivy." An odor highly pleasing to certain individuals may be exceedingly disagreeable to others. The dictionary's definition of a perfume, as "the scent emitted from a sweet-smelling substance; a pleasant odor," therefore does not help us to standardize perfumes, or to prove that all odors which please you and me belong *ipso facto* in that category.

In the absence of any absolute standard of reference, we must fall back upon the verdict implied in the extent of the demand for the different odors and the price which such perfume substances command; a verdict which naturally will vary considerably from year to year, for there are fads and fashions in this field as in others, and will not be identical in different countries, or even among different classes of the population in the same country.

In man, the olfactory cells are located in a recess in the upper back portion of the nasal cavity, away from the direct air current to the lungs. These cells have fine hairlike tips reaching to the surface of the mucous membrane lining the cavity and exposed to the chemical stimuli of odors, while backward from their bases extend long slender sensory nerves which pass through the bone and into the skull chamber and brain stem, there connecting through their end-brushes with the dendrites of nerve cells, whence the stimulus travels to the olfactory area of the cortex, there to be received, interpreted, and the information utilized or filed. These olfactory cells are unique among vertebrate sense cells in being provided with their own sensory nerves, instead of depending upon the sensory axon of an ordinary nerve cell.

To stimulate this organ and produce the sensation of smell, particles of the substance must be brought into actual physical contact with the hair tips of these cells in the mucous lining, either carried by a current of air or by diffusion of the vapor, dissolving in the moisture of the olfactory epithelium and there reacting chemically with the nerve tips; from which it follows that only such substances can possess an odor as are at least partially volatile at the temperature of observation. It has been shown, however, that liquid carriers may also be used, and that odor may be detected when odoriferous substances are dissolved in saline, or other suitable menstrua, and taken into the nostrils. This, of course, suggests the possibility of a stimulus to the olfactory sense by a solution whose solute is itself too difficultly volatile to give off any perceptible fragrance at ordinary temperatures. It is worth noting that in such cases the odor varies with the concentration of the odoriferous substance in the liquid, being quite different in strong solutions from what it is in dilute ones. The theories which postulate odor as due to a form of motion of the ether, and its transmission as similar to that of sound or light, appear to be without any convincing experimental proof.

The olfactory, or first nerve, is hard to investigate because its receptive surfaces are intimately associated with those of the fifth nerve, which is a nerve of common sensation (tactile). For this reason, true smells, *i. e.*, those substances which stimulate the olfactory only, are hard to separate from pungent substances, like vinegar, which stimulate the fifth nerve as well.

For these reasons, Beaunis arranged all substances which affect the olfactory mucous membranes in three groups:[1]

1—Those which act only on the olfactory nerve—(*a*) pure scents, or perfumes, without pungency; and (*b*) odors with a certain pungency, like menthol.

2—Those which stimulate simultaneously both olfactory and tactile nerves, like acetic acid.

3—Those which stimulate only the tactile nerves, like carbon dioxide.

Zwaardemaker,[2] who has studied the subject both extensively and intensively, recognizes nine classes of pure odors, corresponding to Beaunis' first class, which he designates as follows:

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1—Ethereal, or fruity; characteristic in general of the fruits, and due in most cases to the presence of various esters; including also beeswax, and certain ethers, aldehydes and ketones.

2—Aromatic, which is further divided into:

(*a*) Camphoraceous: borneol, camphor, eucalyptol.
(*b*) Spicy: eugenol, ginger, pepper, cinnamon, cassia, mace.
(*c*) Anise-lavender: anethol, lavender, menthol, thymol, safrol, peppermint.
(*d*) Lemon-rose: geraniol, citral, linalyl acetate, sandalwood.
(*e*) Amygdaline: benzaldehyde, oil of bitter almonds, nitrobenzene, prussic acid, salicyl aldehyde.

3—Fragrant, or balsamic, composed of:

(*a*) Floral: jasmine, ylang-ylang, orange blossoms, lilac, terpineol, lily of the valley.
(*b*) Lily: lily, tuberose, narcissus, hyacinth, orris, violet, ionone, mignonette.
(*c*) Balsamic: vanillin, piperonal, coumarin, balsams of peru and tolu.

4—Ambrosial: musk and amber. This odor is present in the flesh, blood and excreta (referable to the bile) of certain animals.

5—Alliaceous, or garlic: onion, garlic and many compounds of S, Se, Te and As; and subdivided as follows:

(*a*) Alliaceous: hydrides of S, Se and Te, mercaptans, organic sulfides, thioacetone, asafetida.
(*b*) Cacodyl fish odors: hydrides of P and As, cacodyl compounds, $(CH_3)_3N$.
(*c*) Bromine odors: Br, Cl, I, quinone.

6—Empyreumatic, or burnt: as in tar, baked bread, roasted coffee, tobacco, benzene, naphthalene, phenol, and products of dry distillation of wood.

7—Hircine, or goat: due in the case of this animal to the caproic and caprylic esters contained in the sweat, and typified also by perspiration and cheese.

8—Repulsive: such as are given off by many of the narcotic plants and by acanthus.

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[1] Stewart, "Textbook of Physiology."

[2] "Physiologie des Geruchs," **1895**, 233.

9—Nauseating, or fetid: as given off by products of putrefaction (feces, etc.), and by certain plants.

Unfortunately, we have no words to represent shades of odor, as we have for colors.

The psychologists, as the result of Henning's investigations, incline to the opinion that there are but six elementary odors:[3]

1—Spicy, found in pepper, cloves, nutmegs, etc.
2—Flowery, found in heliotrope, etc.
3—Fruity, found in apple, orange oil, vinegar, etc.
4—Resinous, found in turpentine, pine needles, etc.
5—Foul, found in hydrogen sulfide, etc.
6—Scorched, found in tarry substances.

and that all others are made up of blends of these six in varying proportions.

Dr. Septimus Piesse maintained that inasmuch as every perfume produces its own peculiar effect upon the olfactory cells, just as every musical note has its own characteristic action upon the ear, therefore all odors can be arranged in a scale or gamut, corresponding to the musical scale; and he actually constructed such a scale of perfumes, each note of the musical gamut having its corresponding perfume, the heavy odors (patchouli, vanilla, etc.) representing the low notes, and the sharp odors (peppermint, citronella, etc.) the high ones. This he termed his "odophone," and asserted that no proper blend could be made unless the component perfumes harmonized in the scale. Thus, the chord of C, for example, would constitute a harmonious blend.

The organic chemist's method of attack upon this problem of classification of odors will be explained a little later. Most of us rest content with just two classes: agreeable and disagreeable.

No sense is more marvelously delicate than that of smell, nor is any more potent in awakening our memories and our emotions. Some people may be indifferent to music, but those unaffected by odors are rare indeed. A breath of perfume brings instantly before our vision past scenes with all their pain or pleasure. Kipling recognized this when he wrote: "Smells are surer than sounds and sights, to make the heart strings crack." From certain odors we recoil instinctively, not because they are intrinsically unpleasant, but because of the associations they recall; while others, perhaps unattractive to our fellows, possess a peculiar fascination for us. The recognition of a perfume is practically instantaneous, as is the picture it conjures up. It is like suddenly glimpsing a familiar face in a passing crowd.

The olfactory cortical center in the hippocampal lobe is known to be widely connected with other parts of the cerebrum, and this probably explains the extensive associations connected with odors, and the excellence of our olfactory memories. In animals like the dog, with highly developed olfactory organs, and among the invertebrates, it is intimately connected with the sexual reflexes, and some remnant of this relationship is found in the human organism. Comparative anatomy reveals the interesting fact that phylogenetically smelling is the oldest sense of all, and it is also true that it gives pleasant or unpleasant sensations in a more marked and general way than either sight or hearing. Of the so-called special senses, it appears to be the one most closely connected with animal appetites, and Howell[4] is led to remark that "over-gratification or over-indulgence of this sense, according to historical evidence, has at least been associated with periods of marked decadence of virtue among civilized nations."

It is also one of the senses particularly susceptible to "adaptation," *i. e.*, a diminution or cessation of the sensation in spite of the continuance of the stimulus, a phenomenon probably akin to fatigue. Both individuals and odors show widely divergent behavior in this respect. Some odors quickly fatigue or benumb the sense of smell in nearly all persons; whereas, with other smells, only a few individuals will gradually lose their ability to detect them while remaining in the same atmosphere.

Drugs that act centrally may stimulate or depress the sensation. Thus, strychnine and caffeine stimulate it, while choral depresses it. The application of cocaine to the nasal mucous membranes totally paralyzes the sense of smell. In disease, changes in the nerve may occur, occasionally resulting in total loss of this sense (anosmia).

The actual amount of an odor which can be clearly perceived by man is in many cases exceedingly minute. Camphor is detected in a dilution of one part in 400,000; musk in 1:8,000,000; vanillin in 1:10,000,000. Vallentine found that 1/120,000 of a grain of oil of rose was all that was necessary; while Fischer and Pentzoldt determined that 1/460,000,000 of a milligram of mercaptan was the approximate minimum amount coming into contact with the olfactory nerves and immediately recognized by them. The pleasant odor of the soil was ascribed by Berthelot, the distinguished French chemist, to traces of an unidentified camphoraceous body, of so powerful a fragrance that even a trillionth of a milligram gave a clearly perceptible smell.

In man, the acuteness of the sense varies widely. Some few individuals appear to lack it entirely, *i. e.*, are smell-blind. It is perhaps surprising to find that, on the average, it is much more delicate in males than in females. By practice, it may be extraordinarily developed, as we see in our own North American Indians, and in some African races and aboriginal tribes, who can track enemies almost like a hound. Among practical perfumers, it is also found cultivated in high degree, especially on the analytical side. A blend, which the layman thinks is a simple perfume, is recognized immediately by the expert as a composite, many or all of whose elements are entirely familiar to him.

One of the beneficent provisions of Nature consists in a sharpening of other senses when some one sense is lost. It is Nature's way of doing her best to compensate for the damage suffered. A group of humanitarian Parisian perfumers are engaged in training men who were blinded in the war to become experts in evaluating odors, not only as a measure of reconstruction, but also in the well-grounded belief that a blind man, freed from any distractions associated with vision, should make a perfumery expert of the first rank.

Yet more amazingly acute is this sense in other members of the animal kingdom. The ability of dogs to follow a scent to which the human nose is wholly blind is a familiar example, as is also the scenting of hidden carrion by vultures at incredible distances. Pliny affirmed that carrion crows have so keen a sense of approaching corruption that they can scent death three days before actual dissolution, and hence sometimes pay the moribund a visit before his time, to avoid disappointment. This is perhaps the origin of the popular superstition that such a visit forebodes death.

The shark, which is among the more active and intelligent of the fishes, has an olfactory membrane which, if spread out, would cover some 12 square feet.

Many insects are strongly odoriferous, and the odors emitted are nearly always disagreeable. Insects also possess a remarkably developed sense of smell, the olfactory organs being located mainly or exclusively on the antennae, in the form of specially modified sense hairs, or sensillae, which are particularly highly developed in insects with the sharpest sense of smell (*e. g.*, in ichneumon flies). Huber has shown that bees are greatly excited by the smell of their own sting poison, and that they dislike musk, but have no aversion to asafetida. Bomare's experiments indicate that the friendly bedbug (*Cimex lectularius*) is attracted, not as popularly supposed by the warmth of the couch, but by the scent of his victim. It is not unlikely that other human parasites and insect enemies, *e. g.*, mosquitoes, gnats, etc., also locate their prey similarly in the dark. The *Arum dracunculus* bears a large liver-colored flower, and exhales a stink which is so fetid and carrion-like that blow-flies, carrion flies, and other slaughter-house frequenters are said to mistake this flower for putrid meat and flock to it from all directions there to deposit their eggs.

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[3] Woodworth," Psychology," 203.

[4] "Physiology," 305.

Some of the most interesting researches are those which have been conducted with ants,[5] insects which can perceive odors either diffused in the air or dissolved in liquids. The tactile and olfactory sensillae are so closely associated on the antennae that when the latter actually touch an object, the ant probably receives both tactile and olfactory stimuli simultaneously, which Forel believes fuse to a single sensation and which he calls the topo-chemical, or contact-odor sensation, and endows the ant with a sense of odor-shape. He explains this by suggesting that we imagine ourselves either blind or in total darkness, but possessed of exceedingly delicate olfactory organs in our finger tips. As we moved about, then, touching various objects, our environment would appear to us to be made up of odors of different shapes, and we would speak of spherical perfumes, oblong stinks, etc. Our mental processes would be governed by a cosmos of chemical configurations, just as they are now by a world of visual (*i. e.*, color) shapes. As ants spend most of their time in the dark recesses of the nest and rely but little upon their eyesight, it is evident that their mental processes must be quite different from our own. These insects also exhibit remarkable powers of odor-discrimination and odor-association, enabling them not only to distinguish the smells characteristic of species, caste, sex, and individual, as well as the adventitious odors of the nest or surroundings, but also (according to Miss Fielde) even progressive odors, due to the changing physiological condition of the individual with advancing age, a refinement which in the case of humans might save us many complications and embarrassments.

The use of sweet-smelling substances appears to have originated in religious worship, to which service they were for some time wholly consecrated, and it is from Persia that we first hear of them. The caravan which carried Joseph captive into Egypt was engaged in this traffic between the latter country and Persia. Alexander the Great, after his defeat of Darius, found in the latter's camp great treasure of perfumes and precious salves.

Among the Jews such material was consecrated to the church, and in the Bible several passages occur where they are rebuked by their prophets for using them upon the person. Sweet balsams and gums are frequently mentioned in the life of our Saviour. At His birth, frankincense was offered Him by the Wise Men, later Mary annointed His feet with precious ointment, and after His crucifixion Joseph of Arimathea placed His body in the tomb with balm and sweet spices. It was this custom which originated our word "embalm."

The Greeks always described their gods as being redolent of ambrosia and, according to their mythology, man would have had no knowledge of perfumes had it not been for the indiscretion of Oenone, one of the nymphs of Venus. As early as 300 B. C., Appolonius wrote a treatise upon perfumes, in which he speaks of essence of rose, iris, and others, mentioning the localities producing the finest quality. The Athenians even had special perfumes for various parts of the body—palm oil for the cheeks and breast, mint for the arms, marjoram oil for the hair and eyebrows, thyme for the neck and chin, but the odor of the violet was prized most highly by them, even as it is with us at the present day. The use of perfumes became such a craze that the perfume shops of Athens were the general rendezvous, where matters of state were discussed, fashions talked over, and stories exchanged, and it was just as natural for an Athenian woman to say "Meet me at the perfumer's," as it would be for a New Yorker to say "Meet me at the theater." At fashionable entertainments the rooms were often perfumed, and occasionally trained doves, whose wings had been previously wetted with the most delightful essences, were allowed to fly about, the vibration of their wings raining perfume down upon the heads of the assembled guests. Solon finally proposed a law restricting the sale of perfumes, so that none should be sold to men, at least; and Socrates bitterly complained because the slave and the freeman, when perfumed, smelt exactly alike.

From Greece, the use of perfumes traveled to Rome, where it was similarly abused. Thus, it is said that Nero, at the funeral of his wife Poppaea, used more perfumes than all Arabia then furnished in a whole year. Pliny raised his voice against such excessive use, and under the Consul Licinius Crassus a law was passed restricting the use of perfume substances, so that the churches should not lack. It is amusing to read that Plancus, proscribed by the triumvirs and pursued by their soldiers, took refuge in a cave, but his hiding place was betrayed by the perfume issuing therefrom.

The overthrow of Rome obliterated the commerce of Europe, and perfumes disappeared from the Continent until brought back by the Moors from Arabia. In this latter country, their use had never ceased, and whole districts were devoted to raising flowers for this sole purpose. The "black-eyed houris" of the Koran, were not to consist of ordinary flesh and blood, but "of purest musk." The Arabian physician Avicenna, in the tenth century, practiced the art of distilling perfumed waters; and in the twelfth century rose water, and possibly others also, was available in large amount, for on the entry of Saladin into Jerusalem, in 1157, the walls of the Mosque of Omar had been previously washed with it.

From the settlements of the Moors, the use of perfumes spread to France, where it soon became general and lavish, reaching its climax at the court of Louis XV, where the royal rooms were perfumed each day with a different odor, and where it was deemed an act of gallantry for a courtier to use the favorite perfume of the lady he courted, just as the knight carried his lady's colors.

Perfumes are said to have been introduced into England by the Count of Oxford, who brought some from Italy in the fifteenth year of the reign of Queen Elizabeth, and their use appears to have been carried to extremes there also, for in 1770 the English Parliament passed a law which provided that "any woman, of whatsoever rank, profession, or condition, girl, woman, or widow, who, subsequent to the date of this Act, shall deceive, entice, or influence to marriage, any of Her Majesty's subjects by the aid of Perfumes, False Hair, High Heels,*****, shall be subject to the same penalty as that now in force against sorcery, and the marriage shall be declared void and of no effect."

To-day the use of perfumes has spread over the world, and has extended to all classes of the community, with a steadily increasing demand. It has given birth to an independent and important industry, regulated mainly, it is true, by fashion and the taste of the consumer, but which nevertheless gives employment to thousands of men, women, and children, urges on the botanist to search for new plants containing odoriferous oils or resins, busies the engineer with devising new machinery for their extraction, and gives to the chemist the fascinating problem of determining the composition of these perfumes and of reproducing or imitating them in his laboratory.

The animal kingdom supplies us with but few valuable aromatics, musk, civet, castor, and ambergris being the only important ones. By far the greater number come from plants, where they occur as the volatile or essential oils, or as the gum resins. The essential oils are contained in various parts of the plant: sometimes in the wood, as santal, cedar, etc.; the bark, as cinnamon and cassia; the leaves, as patchouli, bay, thyme; the flowers, as rose, lavender, violet, tuberose, etc.; the fruit, as lemon, citron, nutmeg; or the seeds, as almond and caraway. As examples of gum resins, on the other hand, we have storax,

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[5] See W. M. Wheeler's "Ants."

Carlile P. Winslow, Edgar F. Smith, Ellwood Hendrick, H. C. Parmalee, R. B. Moore, W. D. Collins, Rev. George L. Coyle, William H. Stone, J. A Steffens

benzoin, tolu, opoponax, olibanum, the latter being the gum usually burned as incense.

The essential oils and other odoriferous constituents are usually obtained from the plant by one or more of the following processes:

MECHANICAL METHODS—In some few cases, the essential oil is present in such large amounts that it can be separated by simple mechanical means. This is true of the essential oils found in the peels of lemons, and of the sweet and bitter oranges. The oil cells may be ruptured by pressure, manual or mechanical, or by perforation with sharp instruments. The process in vogue in Sicily and southern Italy, where labor is cheap, is the "spugna," or sponge process, the peels being turned inside out by hand while pressing against an ordinary sponge. The inversion of the peel breaks the oil cells, and the oil and moisture contained squirts out into the sponge, instead of into the eye of the operator. As the sponge becomes saturated, it is squeezed out, the yield averaging about 1.5 pounds of oil per man per day. In the United States, where labor is high, power presses have been used for recovering citrus oils in California.

The "ecuelle" process of Northern Italy utilizes a saucer-shaped vessel, 8 to 10 inches in diameter, and studded inside with short spikes or knives about one-quarter inch long, and with a half-inch hole in the center, opening into a hollow tube handle some 4 or 5 inches long. As the fruit is rotated in this saucer, the oil cells are punctured and the oil flows down and collects in the hollow handle. Apparatus has also been devised for carrying out the same process mechanically on a large scale.

DISTILLATION WITH STEAM—The proper part of the plant is placed in a still and distilled in a current of steam. This steam may be generated outside the still and passed into it, or water may be added direct to the still contents and the steam generated by boiling the same, or the two methods may be combined. As the steam passes over, it carries with it the essential oil, and the two are condensed and collected together. Insoluble oils or constituents separate from the water in the distillate, while the soluble portions remain in solution in the aqueous layer. Not infrequently, sufficient of the perfume is thus held in the aqueous distillate to render the product of economic value. "Rose water" is such a by-product separated from the insoluble oil or attar of rose.

This is the process by which the vast majority of essential oils are obtained, and is applicable to practically all, although not always giving the best results. It is an economical method, both from the standpoint of the labor involved and the simplicity of the apparatus required, unless the oil present is easily soluble in water, or is relatively small in amount. Further, it is not satisfactory where the perfume substance is itself affected by the steam, as is true with most of the flower aromas. For such odors, one of the following processes is customarily employed.

EXTRACTION WITH VOLATILE SOLVENTS (petroleum ether, benzene, etc.), comprising the four steps:

1—Selection and purification of the solvent.

2—Systematic extraction of the flowers in batteries of extractors.

3—Evaporation of the solvent, leaving a vegetable wax saturated with the perfume (*cire parfumēer*).

4—Recovery of the solvent.

The extracts left after evaporation of the solvent, known also as "concretes," are shaken with strong alcohol, which dissolves out the perfume, these tinctures being then called "floral extracts" (*extraits aux fleurs*). By separating the pure flower oil from its solution in the alcohol, the "quintessences" are obtained.

Using petroleum ether as solvent, the yields of concretes run somewhat as follows, per ton of flowers:

Victoria violets	3.0 to 3.6 lbs.
Roses	3.4 to 5.0 lbs.
Orange blossoms	4.0 to 8.0 lbs.
Jasmine	3.2 to 4.5 lbs.
Cassie	7.0 to 10.0 lbs.
Mignonette	2.6 to 3.0 lbs.

In addition to the flowers mentioned above, extraction with volatile solvents is applied also to tuberose, jonquil, and occasionally to carnations, lily of the valley, heliotrope, narcissus, mimosa, and others.

A disadvantage under which it sometimes labors is the fact that the other substances also extracted by the solvent may affect unfavorably the fine quality of the perfume.

MACERATION, INFUSION, OR ENFLEURAGE À CHAUD—The housewife knows to her sorrow with what avidity butter and other fats, as well as milk (on account of the butter fat it contains), imbibe odors of any kind in the refrigerator, and this property is utilized by the practical perfume manufacturer to collect the aroma from the flowers.

In the maceration, or warm absorption process, the flowers, either in bulk or in fine linen sacks, are soaked in warm (50° to 70° C.) oil or molten fat (lard, tallow, olive oil, etc.) until the perfume is all removed, when the fat is separated, by pressing or centrifuging, and fresh flowers added to it, the operation being repeated (six to fifteen times) until the fat is thoroughly saturated with the perfume. The duration of this digestion varies from comparatively brief periods up to forty-eight hours; generally, the longer the digestion, the greater the yield, but the lower the quality. Fats thus impregnated with perfume come into the market under the name of "pomades," the perfume being then extracted from them by treatment with strong alcohol.

The process is used with violets, roses, orange blossoms, lily of the valley, and some others, but not with jasmine, tuberose, or jonquil, on account of the low yields and inferior quality.

ENFLEURAGE À FROID, OR COLD ABSORPTION—The perfume exhaled by the jasmine, tuberose, jonquil, lily of the valley, and mignonette is best collected by the cold absorption or enfleurage process, the aroma being taken up by thin layers of cold fat or wax. The mixture generally used in southern France consists of 40 per cent beef fat and 60 per cent lard, except in the hottest part of the season, when a 50:50 mixture is preferable. Both fats must be purified with the most scrupulous care, as the character of the resultant pomade depends first and foremost upon the quality of the fats.

The mixture is spread to the depth of about one-eighth inch upon both sides of glass plates which are supported in the middle of open wooden frames, or "chassis," two inches deep, and twenty to thirty-two inches square. The flowers, freed from their calices, are spread over the layer of fat on one side of the glass plate, crisscross furrows having been made previously in the fat, so as to increase the surface exposed.

The frames filled with flowers are then piled up, one on top of the other, in stacks as high as the operator can reach conveniently, thus leaving the flowers enclosed in shallow compartments, the perfume exhaled being imbibed by the fat upon which the flowers repose and by the layer upon the under surface of the glass plate immediately above. The length of exposure varies, being 24 hours for jasmine, 48 for jonquil, and 72 for tuberose. The last named must be placed upon the fat in the unopened condition and there allowed to expand, or it will be spoiled by the next day. After suitable exposure, the flowers are removed, the frames turned upside down, and fresh flowers spread on what was previously the under side of the glass plate, and the frames then stacked up again. By thus alternating the surfaces carrying the flowers, a more even distribution of the aroma in the fat is accomplished. For high-grade pomades, the fat must be exposed to at least thirty different changes of fresh flowers. Where liquid oils are used, instead of solid fats, the glass plates of the chassis are replaced by wire screens which support woolen cloths saturated with the oil.

As before, the perfume is extracted from the pomade with strong alcohol, the small amount of fat so dissolved separated by freezing, and from these purified extracts the essences are recovered by removal of the alcohol.

From the standpoint of the perfume manufacturer, flowers fall into two classes: (1) Those, like the rose and orange blossom, which contain their perfume ready made and immediately available in full amount; and (2) those, of the jasmine and tuberose class, which when first picked appear to contain but small amounts of essential oil, but keep on producing it continuously as part of the life functions of the cell. If flowers of the latter group are treated with steam or hot solvents, they are killed and the further production of perfume ceases; but when the cut bloom is placed over cold fat, it continues to live for many hours and to give off perfume uninterruptedly. So, Hesse[6] found that ten times as much perfume was recovered from jasmine flowers by the cold enfleurage process as by extraction with volatile solvents; in the case of the tuberose, the difference is still greater.

In flowers of the first group, however, larger yields are often secured by the other methods. In the case of orange blossoms, for example, it has been shown[7] that a ton of blossoms yields only 0.2 pound of flower oil to cold enfleurage, whereas maceration gives 0.8 pound, and distillation with steam 2.4 pounds, in the latter case 0.8 pound of this total remaining dissolved in the aqueous portion of the distillate.

For centuries, southern France, with its balmy climate and mountain barriers against the cold winds of the north, has been the world's most famous region for this industry, having succeeded to the position occupied in ancient times by Arabia and its surrounding territory. Even the early Romans were accustomed to bring perfumes from Gaul, and under Louis XII France's export trade in such material was firmly established. Reference has already been made to the lavish use of perfumes at the court of Louis XV, where Mme. de Pompadour is said to have spent 50,000 francs per annum, a fabulous sum in those days, on perfumes alone.

The French Revolution banned such substances totally, but as the years rolled by the wealthier classes resumed their use, and by the beginning of the nineteenth century this use had extended to the middle class also. Since then the development of the industry has been rapid, until to-day its export trade is in excess of three hundred million francs, and is an important contributor to the prosperity and happiness of the French people.

The little city of Grasse, with some twenty thousand inhabitants, in the Alpes-Maritimes Department of Provence, is the heart of the flower-growing district, with a dozen well-known firms and numerous smaller ones, and is really one vast flower garden.

In Grasse alone, the consumption of flowers for the past ten years has averaged in tons per annum:

Orange blossoms	2200	Tuberoses	330
Roses	1650	Carnations	165
Jasmine	1320	Cassie	110
Mimosa branches	880	Mignonette	66
Violets	440	Narcissus	55

In 1898, orange blossoms brought 6 cents per pound, roses 5.5 cents, jasmine 22 cents, cassie flowers and violets 35 cents, and tuberoses 45 cents; but prices have been rising steadily since, and in 1917 (on account of the war) reached 18 cents per pound for orange blossoms and over 30 cents for roses, with other flowers in like proportion. The combined value of the 1917 Grasse harvest of these two flowers alone therefore amounted to nine and one-quarter million francs, or about $1,850,000 at normal exchange.

To produce the 1320 tons of jasmine flowers noted above, at least 750 acres are required, representing some thirty million plants. An orange tree yields about 22 pounds of blossoms, and a violet plant one-twenty-fifth of a pound. A pound of orange blossom oil (oil neroli petal) requires about 1000 pounds of blooms, *i. e.*, the total output of over forty-five trees, or approximately 500,000 separate flowers; while, in the case of the oil or attar of rose, eight tons, or two and one-half million roses, are necessary to yield one pound of the attar. The justification for what seem like exorbitant prices for the highest grade perfumes is thus clear.

In the Department of the Var, adjoining Grasse to the west, some seventy-five hundred acres are devoted to raising violets, hyacinths, mimosa, roses, carnations, lily of the valley, and other flowers, giving employment to eight thousand people, and with an annual output worth between three and four million dollars.

In a large factory, it is not unusual at the height of the season to receive in a single day twenty-two tons of roses and a similar amount of orange blossoms, all of which must be treated immediately before fading; so that men, women, and children work from dawn to midnight during this strenuous period of two or three weeks.

The annual output of lavender oil in southern France has been one hundred tons, worth $600,000; of spike lavender oil, twenty-five tons, worth $50,000; and of geranium oil, five tons, worth $40,000.

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[6] *Ber.*, **34** (1901), 293, 2928; **36** (1903), 1465.

[7] Hesse and Zeitschel, *J. prakt. Chem.*, [2] **64** (1901), 245.

Nearly all of these essential oils are mixtures, and not infrequently contain nonodorous components. They may be used direct, or may themselves be subjected to such treatment as will isolate the more valuable aromatic constituents or remove the inert ones.

The methods for accomplishing this are either physical or chemical.

I. PHYSICAL METHODS. (*a*) *Freezing*—Odoriferous components are often separated thus from essential oils, and the method has the advantage of not changing in any way the quality of the substance so isolated. Safrol can be so recovered from oil of sassafras, anethol from oil of anise, and menthol from peppermint oil. It is a process which is also used occasionally to remove inert constituents (stearoptenes) from such flower oils as the attar of rose, thus effecting an indirect concentration of the odoriferous portion.

(*b*) *Distillation with steam*, to free the more volatile from the less volatile compounds.

(*c*) *Fractional distillation under reduced pressure*.—Many substances which cannot be distilled at ordinary atmospheric pressure without decomposition, boil unchanged when the pressure is diminished sufficiently.

(*d*) *Sublimation*, which amounts to a slow distillation of solids, and is applied in the case of camphor, for example.

(*e*) *Crystallization*, which is the process employed for most solids.

II. CHEMICAL METHODS—(*a*) Acidic compounds may be extracted by aqueous solutions of alkali carbonates, and the acid subsequently liberated from the alkali salt.

(*b*) Phenols are dissolved out by caustic alkalies.

(*c*) Alcohols are often isolated as esters (of phthalic, succinic, or benzoic acids), the esters purified and then saponified.

(*d*) Aldehydes and certain ketones may be combined with $NaHSO_3$.

(*e*) Basic compounds are removed by treatment with dilute acids.

(*f*) Specific reactions are frequently utilized: geraniol forms a compound with calcium chloride, carvone combines with hydrogen sulfides, eucalyptol with phosphoric acid, etc.

(*g*) Methods which will destroy or remove the contaminants without injury to the constituent sought. Thus, in fennel oil the anethol is rapidly oxidized by pure concentrated nitric acid, while the fenchone is practically unattacked; geraniol is not changed by alkalies, but any citral present is thereby polymerized to higher boiling compounds; citronellol is esterified normally by boiling formic acid, but other terpene alcohols are decomposed or dehydrated by it.

The composition of most natural perfumes is now known, at least approximately, to the organic chemist. Some he has been able to reproduce exactly, others he can but imitate. It is his firm conviction that the stimulus imparted to the olfactory nerve tips is due to a definite chemical reaction between the substance of which these nerves are composed and the molecules of the odoriferous compound, and he has endeavored to ascertain whether these compounds have anything in common chemically to which this action may be ascribed. As in the case of the synthetic dyes and synthetic drugs, he has endeavored to fasten the blame upon certain definite groupings of the atoms present in the molecules, and has even christened such groups "odorophores," "osmophores," or "aromatophores." He will tell you that a carbon compound containing one or more such groups in its molecule, if sufficiently volatile at ordinary temperatures, is very likely to possess a definite odor, but what will be the character of the aroma he cannot always foretell so accurately, although even in this direction he has made noteworthy progress. When you see a steeple in the distance, you recognize a church; but only a closer inspection will disclose the particular denomination to which it belongs.

The fascinating nature of this problem lies not only in the discovery of one of Nature's closely guarded secrets, for the perfume has been well termed the soul of the flower, but with this information once in his possession he will be able not alone to duplicate any natural floral essence, but also to build up any number of new ones at will. Already many perfume substances are in common use which, so far as we are aware, do not occur in nature. They are made in man's laboratory, instead of in that of the plant. Many of the well-recognized constituents of essential oils are now produced also by the organic chemist, and the products so obtained are in no respect inferior to the natural article. His lines of attack have been twofold. In some instances, the initial substance has been a natural product, perhaps a perfume itself, which he has transformed by the magic of his art into a more valuable one (*e. g.*, asafetida into vanilla). In other cases, the results are true synthetics, built up step by step from simpler substances, in general obtained from coal tar. The transmutation of this foul black mass into delicious perfumes is one of his miracles, akin to his production of dyes of all the hues of the rainbow and of life-restoring drugs from the same unpromising raw material. Even that deadly war gas, phosgene, has come out from under his hands as a beautiful new violet perfume (methyl heptine carbonate).

Both natural and synthetic products are required by the modern toilet perfume manufacturer. They constitute his raw materials, and are to him what the pigments are to the painter. The preparation of a really fine blend is the work of the expert, and in that occupation he is as truly creating a work of art as are his fellow artists of the brush and chisel. The price which milady's perfume commands is determined therefore not alone by the cost of its ingredients, but also by the skill with which they have been selected and combined to form one harmonious whole.

Informational Needs in Science and Technology

By Charles L. Reese

E. I. du Pont de Nemours & Co., Wilmington, Delaware

THERE is a common saying that "Knowledge is Power." Information and knowledge are so closely related that it might be said that information is power, and coördinated information is power plus. The rapid rate at which knowledge has been and is being accumulated, particularly in science and technology, is brought out very forcibly by the Polish engineer Korzybski in his remarkable book, "Manhood of Humanity," and it seems that extraordinary steps must be taken to coördinate and correlate information in such a way as to make it available to all capable of using it throughout the world.

Efficiency in research and in the application of its results is significantly conditioned by command of information. To the individual, nation, or race which most skilfully, thoroughly, and wisely masters and uses the accumulated knowledge of mankind comes supremacy in industry, if not also in science, politics, and art. Creators of knowledge through the application of scientific method to Nature are prone to belittle or to ignore the devices by which information is conserved, rendered conveniently accessible, and disseminated. Rather it becomes us to inquire whether by giving systematic attention to means of marshaling and using what has been discovered, invented, felt, imagined, constructed, we may not render uniquely valuable service to civilization.

Time was when knowledge was transmitted from man to man or generation to generation either orally or by rude products of human labor. Then came written language and, finally, printing, libraries, and the construction of such keys to knowledge as catalogs, indexes, handbooks, encyclopedias. All the while the rate of accession to information has increased rapidly, although irregularly. Man has become increasingly a thinking animal with remarkable development of curiosity, resourcefulness, originality, breadth of interest and view, foresight, disinterestedness, and sympathy. With multitudes of individuals and generations feverishly active, often progressive, all striving to live more comfortably, happily, usefully and longer, and to command Nature more successfully to these ends, what are the chances that my present idea, thought, or plan is new—shall we say one in a million? It requires but scant attention to the matter to convince us that the efficiency of our use of the products of human thought and of its records is astoundingly low. We chemists are continuously repeating not only mental processes but, as well, the experimental procedures of our predecessors in research. Within limits this duplication of labor is desirable and profitable, but how far we fall short of utilizing as we should the constructive efforts of those unnumbered generations of men and women whose lives prepared the way for ours.

Charles L. Reese

The progress of discovery and invention has nearly eliminated space as a barrier between individuals and peoples. Time, it has been compressed. The output of carefully recorded information is to-day overwhelmingly large—the world is producing millions of printed, typed and written pages of records of research, invention, development, and practical experience, not to mention cultural and esthetic creations. This amazing increase in the quantity of human knowledge is accompanied by corresponding increase in specialization of interest, occupation, and terminology. Tongues also have multiplied, and mental patterns, human needs, and demands have become more diverse. In general, as knowledge has increased, the devices for handling it have become less satisfactory. Few needs are now clearer or more urgent than the construction of efficient informational mechanisms or keys to knowledge. The question I present to you is, "How may the constructive agencies in science and industry help to bring about the designing and installation of suitable informational mechanisms?" May we not profitably bring our scientific method, habit of mind, purpose, and need to bear on this important problem with a view to devising informational master-keys which shall render human knowledge many times more available and, therefore, more valuable?

It is obvious that knowledge, even in a relatively narrow field, has outgrown the capacity of most individuals. However encyclopedic we may be by nature or training, we can master only certain fragments of the information which mankind has accumulated. It is conceivable, however, that we should be able to construct an informational system which would enable every reasonably intelligent and fairly well-educated person to obtain the essential information about a given subject when needed. Why should we not handle the packing, storage, shipping, and distribution of knowledge as efficiently as we manage commercial production? We have gradually devised a system of exchange, national and international, which with reasonable satisfactoriness enables us to enjoy the products of others' skill and industry. Such systems are imperfect, but by comparison with present modes of preserving information and rendering it accessible to posterity, they are highly advanced.

Largely because knowledge is discontinuous and relatively unavailable, history repeats itself endlessly and tragically. Ignorance, it would appear, is responsible for more catastrophes and racial setbacks than are carelessness, selfishness, and maliciousness combined. The solemn duty rests on us to devise adequate ways and means of carrying forward always, with continuously increasing accessibility, the sum of useful knowledge and experience. The fact that the task has not been done is good evidence of its difficultness, not of its impossibility or its lack of importance.

Developments during the War

The World War at once revealed some of the weaknesses of our informational position and our ability to remedy them. When the tremendous need for munitions and men came we were plodding along self-satisfied and generally oblivious of the fact that we commanded relatively little information. Almost over night, investigators and industries became aware that knowledge, conditions, discovery, invention, production—in a word, efficiency of effort was lacking. Intelligence bureaus, informational departments, staffs of abstractors, indexers, compilers, and purveyors appeared suddenly all over the country. What Germany had at hand in 1914, because of her superior foresight and appreciation of the supreme value of systematized available knowledge and of the indispensableness of research, we were compelled to try to create at high speed and with feverish haste. It is enlightening to examine some of our information-seeking activities in their relation to our present need and opportunity.

COMMERCIAL ACTIVITIES—My own company, when it undertook a number of new lines of manufacture, beginning during the latter days of the war, recognized the need of more extensive and more comprehensive information along these lines. An Intelligence Division was therefore organized, charged with the collection, integration, and dissemination of technical information on the subjects in which we were interested. At the time of its maximum activity this Division was spending $80,000 per year for salaries alone, and comprised a personnel of thirty-five men and women.

A classified index of the dye patents of the United States was prepared; foundations were laid for a general information catalog, which, while no longer being added to at the present time, is still a valuable library tool; an information index of our research reports was started and is just being completed; a library was organized, etc. While many of the activities of the Division probably were of interest only to the du Pont Company, it is unquestionably true that some of the activities could better have been carried on by some organization like the Research Information Service of the National Research Council, and the results would then have been available to the country at large.

For more than five years the Chemical Catalog Company has conducted an information bureau for the benefit of chemical industry and its personnel. Informational demands increased so considerably that it was found desirable in 1921 to place this bureau on a charge basis. A fee of $25 per year is now charged to firms or individuals who wish to command the service. This also, it should be noted, is a highly specialized service limited to chemical technology and making no special provision for information concerning research.

The National Industrial Conference Board, organized and maintained by the industries of the country, is one of the most active and efficient intelligence agencies in the country. Their activities are mostly along industrial, social, and economic lines, and they have made since 1917 forty-five research reports and twenty special reports as a result of studies on such subjects as changes in cost of living, strikes, works councils, profit sharing, health service in industry, taxes, hours of labor, and metric versus English system of weights and measures. All of these are the results of the collection of statistics and the presentation of facts.

These instances of informational activities directed toward increasing the availability of commercially valuable information are typical of what has been achieved or attempted for various industries throughout the United States since 1917. Many of the informational bureaus which sprang up by reason of war needs have been abandoned because of economic pressure. Others are struggling to achieve self-support and profit. The indications are clear, however, that a general informational clearing house should be an endowed public service organization, independent alike of the need of self-support and of gain.

GOVERNMENTAL WORK—Of governmental informational activities certain notable instances should be mentioned. The Food Administration perfected a staff and statistical machinery which provided it with unprecedentedly complete intelligence concerning food production, distribution, consumption, waste, and prices. The statistical department of the Food Administration, as was generally recognized during the war and has since been made clear by its reports, functioned with marvelous efficiency as an intelligence agency.

With a view to enabling the Federal Government to command such available information as was essential for wise action, a central bureau for planning and statistics was organized and, at the height of the need, operated for several months. But as soon as the need began to diminish this admirable idea and its initial expression were abandoned. Thus was once more exemplified the general inability to appreciate the importance of providing organization and apparatus to make human knowledge readily available.

In the Army and the Navy, intelligence services, with the advent of war, emerged from dark corners and spread knowledge-seeking tentacles throughout the world. Rapidly these military bureaus evolved systems of gathering, classifying, and distributing information of essential importance to a nation at war. For a time the military departments were immersed in positive and negative intelligence, much of which doubtless was generally available to enemies as well as allies. Probably it will require years for these protective and defensive intelligence services to sink again into that oblivion which ignorance of world conditions tends to encourage. Seemingly, the more ignorant a nation, the safer it feels; and certainly the more ignorant an individual the less he appreciates the possible values of knowledge and of instrumentalities for commanding it.

NATIONAL RESEARCH COUNCIL—Last, because it is first in our interest as investigators, mention may be made of the informational work of the National Research Council. This was begun while the Council served as the Department of Science and Research of the National Council for Defense. At first there was organized a Research Information Committee with headquarters in Washington, and offices in London, Paris, and Rome. The principal and important function of this committee was to gather information about current research of military significance and to distribute reports of such work to appropriate military and civilian agencies. The committee served, through its staff of scientific directors or attachés, primarily as an information gathering and disseminating agency. Its success led to subsequent reorganization as the Research Information Service, concerning which more will be said later.

The various informational activities which have been selected as examples of types are all of them indicative of the need and opportunity which, compelling during the Great War, are always with us and are far more worthy of serious study and effort than is generally realized.

THE WORLD SITUATION

It has already been hinted that there was rare appreciation of the importance of human knowledge during the war and that we already are tending to lose this appreciation. With this observation in mind, it may prove worth while to make a hasty survey of the world situation.

GERMANY—Germany has the instrumentality for commanding scientific and technological information and for stimulation and guidance of research effort which all but gave her victory. This instrumentality, whose principal locus is Grosslichterfelde, includes the great national laboratories and the informational bureau which has quite naturally, but by no means accidentally, grown up in connection with "das königliche Materialprüfungsamt." The purpose of this institution, which was organized at Charlottenburg in 1871 and in 1904 moved to its present site, is to place at the service of the German people a staff of thoroughly competent specialists, armed with all technical facilities and records of human progress. This staff holds itself at the command of investigators, inventors, manufacturers, technologists, agriculturists, to assist in the solution of their practical problems and to help them to command the accumulated knowledge and progress of the whole world. This institution is said to have claimed to be able to answer 80 per cent of the problems put up to them supposedly demanding experimental research.

We may not reasonably flatter ourselves with the thought that we are exceptionally advanced in our consideration of informational needs and opportunities, for the chances are that in Germany, Japan, and probably other countries as well, plans have already been formulated, and possibly are well advanced toward practical expression, for the effective command of world informational resources in the interest of national development and prosperity. But whatever we do toward improving our informational resources, we can least of all afford to forget that as a nation we are backward in supporting, dignifying, and so far recognizing the values of constructive work that it necessarily commands the respect, attention, and confidence of our people, and is regarded as essential to human progress.

Yet, Germany does not stand alone in appreciation of informational need or in determined effort to meet it. England, years ago, was chief mover and responsible agency in the organization of the International Catalog of Scientific Literature, an ambitious project which ultimately failed because it was modeled too closely after the librarian's ideal of an index to knowledge. The Catalog, although undeniably useful as a list of all scientific publications, did not prove satisfactory to investigators and consequently failed to command their support. Its fate points a lesson which it is hoped we may heed, namely, that a mere catalog of titles is an entirely inadequate key to human knowledge. It demands supplementation, transformation, or both.

BELGIUM—Belgium also has witnessed an attempt to list and partly to summarize all published documents. In effect, this amounts to the construction of a classified card catalog to which one might turn with reasonable expectation of getting useful references or suggestions concerning almost any topic of human interest. This project also has suffered the ills of war and is moribund. We well may ask whether the plan was wisely conceived and whether, however thoroughly it may be carried out, it can reasonably be expected to meet our principal informational needs.

As has already been indicated, America, although full of informational agencies—industrial, scientific, political—has no general informational clearing house for all interests. Special informational bureaus or intelligence services come and go so rapidly that a directory cannot be kept to date. Washington is crowded with invaluable sources of information covering the entire range of human interests and activities. There are scores of federal offices, bureaus, divisions, departments which command useful information; but there is no individual and no bureau which serves as guide or directory. Consequently, the search for information in the great national center of intelligence is likely to prove baffling, discouraging, and, at worst, irritating. What could readily be done for informational Washington by the creation of a central clearing house, what indeed already has been attempted for quite another purpose by the Bureau of Efficiency, certainly should be done at once and with the greatest human foresight and skill for our entire country, for the world, because the isolated or independent nation is a fiction, and for the whole of human knowledge, historical as well as current. Nowhere in the world, so far as present information indicates, is there in plan or operation an informational clearing house conceived on a large scale with intent to render the whole range of human information increasingly accessible and useful. It is precisely such an informational organization that our times, our industries, our investigators, our public institutions, our public servants, and our people need. The realization of need in most quarters is not yet compelling, but in others it is definitely sensed and it is believed that the time is ripe boldly to extend the plans of the Research Information Service of the National Research Council.

W. W. SKINNER

CHARLES L. PARSONS

RESEARCH INFORMATION SERVICE, NATIONAL RESEARCH COUNCIL

From the Research Council's committee on research information, following the Armistice, was organized a division of the permanent Council called the "Research Information Service." It was my pleasure and responsibility to assist in planning, organizing, and furthering this informational agency. The Service has now been available for three years. During the first two years attention was centered on the study of the informational situation, the formulation of plans, and the creation of fundamental informational tools. From three years of effort to discover, understand, and satisfy informational demands, certain principles of organization and policy have appeared. These have been carefully considered by an organizing committee which is representative of research interests and of the principal industries and types of informational agency of the country. Foremost among the principles agreed upon by this committee on organization are the following:

1—The desirability of developing initially a general clearing house for scientific and technological information rather than a mere storehouse or depository of knowledge.

2—The conduct of a free informational service for the promotion of research, useful applications of its results and the supplying or disseminating of knowledge necessary for or beneficial to human welfare and progress. It is recognized by the committee that there is a practical limit to the possibility of free service beyond which charge sufficient to cover the cost of service should be made.

3—The encouragement and fostering of a miscellaneous request service initially limited to scientific and technological knowledge which shall strive to supply reliable information concerning any aspect or relations of research. Especially to be mentioned in this connection is information concerning research problems, projects, methods, processes, results, current work, laboratories, equipment, apparatus, funds, and other means of support, persons engaged in constructive or creative work, publications, and bibliographies.

4—The primary task of the special staff of the Research Information Service is set forth as the designing and construction of informational keys, instruments or tools essential to the efficient functioning of a clearing house for human knowledge. The final purpose in endeavoring to create informational instruments is the development of a complete coördinated machinery for gathering, classifying, locating when needed, and disseminating trustworthy information.

5—Utilization by the Service of correspondence, informational publications, and publicity as ways of meeting the informational needs of organizations and individuals, and of educating the public to appreciation of the possible values of a carefully planned and efficiently conducted informational clearing house.

The group of men, among whom appear several of our chemical colleagues, which has been chiefly responsible for the launching and development of this project naturally has come to look upon it as America's most ambitious, most thoughtful, and most promising attempt to be useful in a large way and permanently in connection with the handling of the varied and multitudinous products of human thought and ingenuity. Dr. James R. Angell, first chairman of the post bellum Research Council, once characterized the painstaking, albeit somewhat discouraging, labors of the Research Information Service Committee as primarily an "investment in brains." He believed firmly in the wisdom of this investment and in the supreme importance of the Council's informational opportunity.

To repeat, even casual observation serves to indicate the scattered and special character of sources of knowledge and the extreme improbability that a needy individual will happen upon the right source. It is only by happy accident that one locates satisfactory information outside the field of his special interest and activity. There is neither correlation nor coördination; there is not even a central medium of communication to place those who desire information in touch with those who have it. It is proposed, therefore, to make the Research Information Service of the National Research Council a great clearing house for informational requests and thus to increase the availability and value of existing sources and to supplement them as necessary. The Service will not strive for encyclopedic knowledge, save of sources, but undoubtedly its files will gradually acquire value. Ultimately it may become a great informational center, as well as clearing house.

EDWARD BARTOW

PERCY H. WALKER

Although at present the Service is rather strictly limiting its activities to the natural sciences and their practical applications in industry and engineering, it is proposed to direct its development along those lines which promise to promote both increase of human knowledge through constructive effort and improved availability of knowledge already achieved. Once suitable clearing-house machinery has been designed, constructed, and perfected, there is no obvious reason why the plan which has been outlined should not be applied to the entirety of human knowledge.

Although it is commonly believed that the important products of human skill and labor are satisfactorily transmitted from generation to generation it is important to note that this is not true of those products of mental labor which gain expression merely in written language. Useful inventions, commercially developed, are not likely to be lost except by replacement, but verbal descriptions of discoveries or inventions which have not achieved material expression are very likely to become buried in our great informational storehouse, our libraries. In the light of this condition, it has seemed peculiarly important to develop an informational service to supplement the library. This evidently means new types of keys to knowledge. The staff of the Information Service has planned and begun to develop files for research personnel, problems, results, laboratories, methods, procedures, experimental equipment, and bibliographies. It is surprisingly easy in this kind of venture to design special equipment which cannot be operated successfully because of its needless complexity, size, or costliness. The tendency is always toward specialization and against the creation of efficient clearing-house machinery.

It is now pretty generally recognized that the first and most important step toward increased availability of information should be the preparation of reliable objective, analytical abstracts of literature, and the construction of detailed subject indexes. If the scientific and technological literature of the world were regularly and systematically abstracted and listed, and if all this condensed information were available in the Research Information Service, it is reasonable to anticipate that from 70 to 90 per cent of all requests could be answered directly and with reasonable satisfactoriness from this single master-key. Were this proposed key to published materials supplemented by files of records concerning current research, scientific and technological workers, laboratories—their construction, equipment, etc., it is certain that many more requests could be successfully answered.

The Service has undertaken to develop, as its fundamental tools, first, a list of informational sources including individuals as well as organizations, specialists as well as informational bureaus; second, it is building up a library of source books which it is hoped may ultimately become an invaluable master-key to published information. Scarcely less important than these two types of key for clearing house use is the research personnel file which is counted upon to supply reliable information concerning all research workers, their resources for research, their interests, and their principal lines of activity. This file already contains nearly 14,000 names and is being mechanized by the use of the Findex system for convenience and accuracy of sorting. It is cited merely as an example of a type of master-key which, if skilfully planned and efficiently developed, an informational clearing house is sure to find entirely essential and of steadily increasing value.

As is true in many other directions, the best way to appreciate the problems of an information service, its need, and the value of devices for meeting them, is to try to use the Service and to follow as closely as may be the functioning of the clearing-house mechanisms in supplying information.

American chemists are far better situated informationally than are most other groups of scientists or technologists. Similarly, the chemical industries have been conspicuously more progressive in their efforts to command scientific and technological information than have other commercial interests. To what extent this is due to the necessity created by German initiative and resourcefulness is difficult to determine, but certainly the German influence has been considerable. And with all its provisions for marshaling and promptly commanding pertinent information, it is clear that American chemistry is not in the strongest possible position and that it still must reckon with species of ignorance and forms of competition which are as inimical to national welfare as they are to professional progress. It is entirely fair to ask, "Would not systematic, sustained, intelligent study of informational needs and values be likely to result in great improvement for chemistry?" My own observations and experience in connection with our Chemical Intelligence Department indicate an affirmative reply.

GETTING ON TRAIN AFTER VISIT TO ISHKOODA IRON MINE, ON INDUSTRIAL EXCURSION

Chemistry and chemists, as well as those who as laymen seek chemical information, undoubtedly can profit greatly by a wisely planned and efficiently conducted general informational clearing house. We especially need such a service to facilitate contacts with related fields of research and with discoveries, inventions, and developments which, although not chemical, have significance for our special interests. We need such a general clearing house also to increase our profitable contacts with the consuming public. We need it to supplement our own keys to chemical literature, our abstracts, indexes, compilations of information, and even our special informational agencies, such as the Chemical Catalog Company, for through the sort of national informational clearing house which the Research Council is undertaking to create our special informational aids in chemistry will be made available to untold millions of scientists, industrialists, and consumers of chemical products.

It is greatly to be desired that ultimately an international service of this character be established with not a single locus, but with branches in most of the important countries, containing on file in each all of the material collected, so that in case of a cataclysm such as has befallen Russia and which might have befallen all of Europe if the World War had lasted much longer, it would not result in the loss to the world of a large part of her wealth of information. Such an arrangement if it were possible would require governmental coöperation but would result in a tremendous saving of effort and be all-embracing.

The Research Information Service of the National Research Council is a public service agency. It is ours to make or to mar, to use or neglect. It urgently invites our coöperation and freely offers its aid to us individually and collectively. We cannot afford to do less than interest ourselves intelligently in this difficult undertaking whose possibilities of usefulness are almost limitless and to endeavor to aid in so directing its further development that it may command our support increasingly.

Before closing I wish to call attention to the valuable results already accomplished by the Research Information Service of the National Research Council, due to the untiring and invaluable efforts of Chairman Robert M. Yerkes, at whose suggestion this paper was prepared.

Recent Developments in the Chemistry of Rubber

By William C. Geer

VICE PRESIDENT, THE B. F. GOODRICH COMPANY, AKRON, OHIO

RUBBER as it appears to the consumer in the form of tires, hose, or rubber overshoes is not a chemical individual derived by the operation of chemical processes nor is it the crude rubber of nature. The rubber articles are made up from one or more of thousands of mixtures, each composed of several different substances. These substances are made into mixtures by mechanical means, and to give them the physical properties required each must be submitted to the one chemical process of the industry, the action of temperature and time known as vulcanization. To attain highest values, the chemistry of these raw materials, of the vulcanization operation, and of the finished mixtures has been diligently studied during the past few years. From this study have come some interesting developments.

EARLY DEVELOPMENT

While rubber was made known in its raw or crude form to the Europeans by Columbus, and other explorers in the sixteenth century, it remained until the third decade of the nineteenth century for a phase of its chemistry to be recognized in a practical way, and only within the past few years have chemists come to reasonable conclusions with respect to the mechanism even of this fundamental reaction. You may pardon me, therefore, if I refresh your memory with some of the older and to rubber men, well-known ideas, in order to pave the way for a brief discussion of the new.

The raw rubber is a vegetable product derived from the milk or latex which flows after cutting the bark of certain trees which grow profusely in a belt about two hundred and fifty miles each side of the equator in countries where the soil, rainfall, and climate are propitious. Spaniards in the sixteenth century saw South American natives spread this latex upon crude fabric. The crude rubber layer thus formed served as an excellent waterproofing medium. The first rubber shoes were made by the Indians, who poured latex over clay lasts and dried it in the smoke of a fire. Men, like cats, abhor wet feet, and shoes are really our earliest useful application of rubber.

The dried product, as a brown, frequently evil-smelling body, came into Europe in the eighteenth century. From then on, chemists and practical men studied this product in the attempt not only to determine its composition but also to find ways and means of utilizing it. Priestley named it, Faraday analyzed it, Hancock found uses for it, but there were fundamental difficulties which restricted its use and caused many thousands of articles to be returned to the manufacturers. The rubber was found to "dissolve," as it was termed, in turpentine and coal-tar naphtha. This solution or cement was spread upon cloth to make raincoats. It had, however, the disadvantage of being sticky and of softening with heat and stiffening with cold. Even the milder climate of England, but especially the heat of our American summers, caused the coats to fall apart and to stiffen so decidedly when worn in the winter that they became virtually like tin armor. An early story has been told of a man who wore one of these coats in the winter in New York, who, finding the garment so stiff that it was difficult for him to get around with it on, came in and sat down in front of a hot fire in order to soften it. It did soften and too much so, for it became necessary for friends literally to cut the garment from him. Investigators with scientific as well as only inventive training made efforts to dry and stiffen the product, and this led to the development of mixing machinery. The rubber mixture was thus developed.

One early practical man, Hayward, conceived the idea of dusting sulfur upon the surface of rubberized cloth and submitting it to the action of sunlight; he found a drying action on the surface but no change in the effect of heat and cold. One day a hardware merchant who had failed in business but who was of an inventive turn of mind, Charles Goodyear, was attracted to the window display of a rubber company in New York, where he saw life preservers made of rubberized fabric. One thing led to another, and he was stimulated, as he says in his memoirs, to study means for eliminating the undesirable effects of temperature. He learned of the Hayward patent, purchased it, and began experiments with the mixing of sulfur into this crude rubber. Finally, to tell his own story, he observed one day in January 1839 that certain mail bags which had been returned by the Government, the rubber part of which consisted of a mixture of rubber, sulfur, and white lead, had not softened after standing for some time in the vicinity of a hot stove. Without scientific training, but with the instincts of an investigator, he at once was led to further experiment as a result of this observation. He made numerous trials until he came clearly to the conclusion that time and temperature with a rubber-sulfur mixture were the two controllable factors which would cause a change in rubber by which it would remain flexible in the cold and not melt when heated. This process was later named vulcanization. Vulcanization, however, changed not alone the hardness under changing temperature conditions but altered a number of other physical properties. The breaking or tensile strength, which is a most important property for industrial and service uses, was increased.

WILLIAM C. GEER

I have mentioned this incident in the history of rubber, purely to give credit to those early scientific minds, for we all know how many of the greatest discoveries in the laboratories of the scientists, in the practical work of the factories or even in the crude workshop of an untrained inventor, are due to keenness of observation. If young men under training or who are at work in our factory laboratories could only learn that at least one fundamental for success is the faculty of keen observation to see leads into new territory, how much faster would our research work proceed! Goodyear not only discovered the fact of an interaction between rubber and sulfur, but he also discovered and described in his patent the first accelerator of vulcanization, the Dutch process white lead.

The growth of the rubber industry from its meager output of $7,000,000 worth of products in 1850 to $1,122,000,000 worth in 1919, all of this being based upon this fundamental principle, is one of our striking industrial achievements. These facts of early history show how close should be the connection between mechanical invention and chemical research. Chemists are quite justified in using the term "research" for their part of such coördinate enterprise. The inventions of the early workers failed to develop the rubber industry. I think we must call Goodyear a chemist, although he was not trained as such; but sometimes men become chemists or physicists, or even financiers, without training.

CRUDE RUBBER

Let us go back now and trace step by step rubber as it grows in the tree down to its use in practical products and discuss some of the recent developments which give us a deeper insight into the chemistry of these various processes. Through the researches of DeVries and others our knowledge of the chemistry of the latex and of raw rubber has come to scientific exactness. Rubber latex is a colloidal suspension. It exhibits the Brownian movement, and under the microscope the size of the particle is approximately 0.0005 to 0.003 millimeter. These globules are not always spherical. Since it has characteristics of a solid it is reasonable to suppose that crude rubber is produced in the tree in glands or cells which put it into the watery fluid or serum of the latex in solid form.

An average analysis of the latex shows it to contain the rubber hydrocarbon as its chief constituent to the extent of 28 per cent, 1 to 3 per cent of resins, mineral matter, sugars of several kinds about which little is known, proteins, if we may call the nitrogenous matter by this general name; the balance, about 60 per cent, is water. Commercial rubber includes several of these substances and so exists to about 30 to 35 per cent in the latex. It is highly probable, in view of the action of different grades of commercial rubber, that the resins are in solution in the rubber hydrocarbon; it is pretty definitely known that the protein plays the part of a protective colloid. There is an interesting field for colloid study here, for the protective action of these proteins in the latex is different in different species of trees. That from the Hevea tree does not cream on standing nor can these fine particles be separated by any centrifuging process that has yet been applied to it. On the other hand, the latex from other trees, notably the Castilloa, will cream with relative ease, and rubber may be separated by mechanical means. We may possibly compare the percentages which have been given with that of milk in which the butter fat runs only from 3 to 6 per cent, and the proteins from 3 to 4 per cent, and which readily creams on standing.

Rubber latex, the moment it comes from the tree, begins to change; the action of bacteria is rapid, probably first affecting the proteins, changing them to amino acids, amines, and various other decomposition products. It is highly important in the practical handling of latex to carry it to its first manufacturing step before these bacteria can make too great an alteration in this liquid; otherwise crude rubber of different colors and physical properties would result with consequent lessening of its value in the markets.

COAGULATION—The first step in the manufacture of crude rubber consists in coagulation, around the study of which there has been a great deal of scientific work. Investigators have found, as those who understand colloid chemistry would expect, that dilution of the latex to a standard rubber concentration is the first fundamental, and the second one is the breaking down of the protective action of colloids by means of acid of the right concentration. Various acids have been tried: formic, sulfuric, hydrochloric, and others. Various electrolytes have been used, but up to the present time a concentration of about 1 per cent (in terms of rubber) of acetic acid gives the best product.

Coagulation is known to be a simple massing together of the rubber globules. The rubber itself is not changed, and as a result of this addition there is formed at first a soft, white dough which, when congealed enough to be capable of practical handling, is washed free from serum, acid, and other substances upon a washing mill. About 95 per cent of the rubber now prepared on the estates is made by the acetic acid method, which gives a crude material of good appearance. When made in this way and where discoloration is prevented by small quantities of sodium bisulfite, there results the "pale crepe" of commerce. When, however, the sodium bisulfite is not used, and in addition an attempt is made to imitate the smoky odor and appearance of the original Brazilian grade by a smokehouse process applied after the rubber has been washed and partially dried, there result the "smoked sheets" of commerce.

There are many unsolved problems of a mechanical as well as of a chemical character. A most excellent grade of crude rubber has come into the market in recent years which is prepared by the total evaporation of the latex. This has good properties, although not greatly different from that prepared by the method already briefly described. The real field here probably lies in a study of the action of polymerizing chemicals, for there is no better place to submit a substance to chemical action than when it is in its most finely divided state. Some day enterprising chemists, either of the rubber factories or in connection with the government experiment stations or private estates, will study substances to be added to the latex to serve as polymerization agents prior to coagulation to give us grades still better than we now receive.

CULTIVATION—The cultivation of rubber trees on plantations or estates is the result of an idea of the Englishman, Hancock, who suggested it in 1856. It was carried to completion by another Englishman, Sir Henry Wickham, who in 1876, with the support of the officials of the Kew Botanical Gardens, succeeded in shipping out of South America some seeds of the best tree, the black *Hevea brasiliensis*. The seeds were planted in the Kew Botanical Gardens. The young sprouts were sent to Ceylon; seeds from these trees were sent in later years to Sumatra and the Malay Peninsula. From then on, the rubber plantation industry has grown, and it only remained for the tremendous demand incident to the use of crude rubber to support the automobiles of the world, until an industry which produced but four tons in 1900 developed a production of 304,000 tons in 1920. Over seventy-five per cent of the total world's product comes to America. To supply the world with 300,000 tons of crude rubber requires about 270,000,000 gallons of rubber milk. Of these tons which come into America, about 75 per cent are used in pneumatic tires, solid tires, and inner tubes. Probably one-third to one-half of the world's production comes to the city of Akron, Ohio.

There were under cultivation only 116,000 acres in 1905 and over 3,000,000 acres in 1920; over 70 per cent of this acreage is owned by British capital and about 66 per cent of it is under the political control of Great Britain in her Colonies. As a result of the tremendous demand in 1910 and the over-supply in 1920, the price of this material fell from $3.00 a pound to about 13 cents a pound. When one considers that the cost of production of plantation rubber varies from 18 to 25 cents per pound, it is obvious that additional ideas for its use in new articles will be most welcome. In the economics of rubber illustrated by these figures, London is to-day the financial center, the city of Singapore on the Malay Peninsula the shipping center, and Akron the manufacturing center.

COMPOSITION—This plastic raw rubber is shown by the best analyses to consist of the rubber hydrocarbon 92 to 94 per cent, 1 to 4 per cent of moisture, mineral matter, resins, and proteins; in other words it is not far from the composition of the latex, with the exception of water and water-soluble ingredients. Ultimate analysis shows the composition of the rubber hydrocarbon to be $(C_5H_8)_x$. On account of the supposed relation of rubber to the true terpenes, we customarily think of it in terms of the formula $(C_{10}H_{16})_{x/2}$. The structure of the hydrocarbon has been subjected to much controversy. Chemists now generally agree. Isoprene, C_5H_8, is a methyl derivative of butadiene. This butadiene hydrocarbon consists of a chain of four carbon atoms with alternate double bonds, or a conjugated system of double bonds. Addition to such a system takes place at the ends and causes the formation of a double bond in the center. We believe that the polymerization of isoprene to rubber consists in the addition of one molecule to another in

W. Lee Lewis, Charles L. Reese, Van H. Manning, John E. Teeple, William McPherson, Francis P. Venable, Martin H. Ittner, B. R. Tunison

this way, forming a succession of these groups linked together into a ring of uncertain dimensions. How far the chemical composition or state of polymerization, or the state of aggregation of the polymerized magmas affect the properties of crude rubber as we know them, and how far the hydrocarbon from trees of various ages differs chemically and physically are all unknown phases of this interesting problem. We do not know the part played by mineral substances nor the exact condition of the nitrogenous matter, although the proteins have a most important influence upon the colloid characteristics of the rubber.

Much study has been made by some chemists in the analysis of rubber to determine the percentage of acetone-soluble matter. Rubber from different botanical species varies largely in resins. Vulcanized rubber changes on standing, owing to the formation of acetone-soluble oxidization products. The rubber resins are highly complex and whether they were the original source of rubber in the tree or whether they have been produced from the rubber we do not know. The acetone extract is probably to-day the one reasonably reliable means of determining the botanical origin of different grades, and the fresh from the deteriorated rubber, although the control of quality in a finished article can be carried on irrespective of the origin of the rubber, and the amount of acetone extract is not, as some have believed, a guide to quality of a vulcanized rubber mixture.

The chief chemical property of the rubber hydrocarbon is unsaturation. It adds directly halogens, halogen acids, sulfur, and sulfur chloride, as well as certain other substances.

The story of synthetic rubber has been much discussed. Synthesis of it is a well-known fact. Much work was done upon it during the war, in Germany, where considerable quantities were produced, but it was not the same hydrocarbon as that derived from the tree. It was a close relative known as methyl rubber. However, the tires and other soft rubber articles made from it were decidedly inferior in service. It was, however, valuable in hard rubber or ebonite.

Colloid Chemistry

The study of the colloid characteristics of raw rubber constitute an important field in which our knowledge is growing. Consider that the latex contains innumerable very small solid particles surrounded by a protective colloid. On massing the rubber together there is reason to believe that a definite structure remains. The rubber is probably still surrounded by the film of protective protein colloid, or in any event the interfacial tension between these particles when massed remains great enough to have an appreciable effect upon the properties of the substance. When rubber is softened, or as we call it masticated, upon a mixing mill, even with the minimum of heat, a change occurs, in which probably the protective colloid is broken up and mixed with the rubber, without, however, radically altering its vulcanization properties. A cement of softened or masticated rubber in benzene is thinner than one made of unworked crude rubber. This phenomenon could lead one to believe that this crude rubber may contain a structure which can be broken down by mechanical action but not by the method of absorption in a solvent. When a sufficient amount of it is placed in a solvent it swells, showing absorption of the solvent by the rubber, and only after a long period of time will it become a viscous solution or cement. Indeed to gain uniformity it is necessary to beat it up. Yet in this form it is not a gel and does not show the phenomenon of syneresis. These data seem to indicate that a benzene rubber cement is therefore simply an emulsion of benzene dissolved in rubber as one component, dispersed in benzene as the other component.

Some interesting studies by Stevens in England on vulcanization in solutions are presenting some leads into the colloid chemistry which if followed may give us information of marked value. It has long been known that when vulcanized rubber is placed in solvents it does not dissolve but merely swells, the swelling action being one and one-half times in ethyl ether, nearly double in benzene, and about two and one-half times in chloroform. Swollen vulcanized rubber is weak but may on standing lose the liquid by evaporation and return to its original size. Stevens, however, has vulcanized a rubber sol to a gel, which on evaporation of the dispersion medium he states yields a soft vulcanized rubber of normal properties. This he has done by the cold or sulfur chloride vulcanization method, working with benzene solutions of masticated plantation rubber. He has formed gels almost immediately. Syneresis sets in and the gel contracts, expelling the solvent which contains little or no dissolved rubber. He has also obtained vulcanized rubber sols by heating raw rubber sols in a sealed vessel under pressure. These on spontaneous evaporation yield films of vulcanized rubber which cannot be redissolved in rubber solvents. There is much of interest to be determined from a pursuit of this field.

Absorption of Light

The absorption of light by crude rubber has recently been investigated by Lewis and Porritt, who find no decisive evidence of absorption bands, but a general absorption which is fairly strong for wave lengths below 2700 but rapidly diminishes with increase in wave length. It may be that this investigation will give us further evidence and an explanation of why the rubber is so rapidly oxidized in the presence of ultraviolet light.

Diffusion of Gases

The early studies of crude rubber with respect to diffusion of gases through it have recently been worked out on a scientific basis for both crude and vulcanized rubber by Venable and Fuwa, who examined two grades of crude rubber and two vulcanized compositions. This work was stimulated by the use of rubberized balloon fabric during the war, and these investigators made a most interesting and valuable contribution in relation to balloon work. The amount of gas thus held in the rubber was directly proportional to the pressure, and unaffected by the degree of vulcanization or the presence of compounding ingredients. They verified the customary assumption that the mechanism by which a gas penetrates a rubber membrane is through diffusion of the gas, which is held in true solution. This, it is to be hoped, will lead to a further investigation so far as hydrogen and helium penetration are concerned, to find components which will reduce the solubility of these gases in rubber mixtures. Could we use in dirigible balloons a rubber mixture highly insoluble toward hydrogen and helium a great advance could be made.

Another problem in this field is the development of a rubber mixture in which war poison gases are insoluble. Our Washington friends may agree to abolish poison gases from warfare. We should, however, be active in preparation of methods of defense against it. We are forbidden to carry concealed weapons, but there is no law of God or man to prevent us from the use of locks on our doors and bolts on our windows.

I would earnestly recommend to the American Chemical Society the extension of gas defense research to investigate gas mask and other protective clothing, alone as far-sighted patriotic citizens if coöperation with the War Department be not allowed. It is a field in which research work of a coöperative character can be undertaken, with who knows what valuable results to us in the future.

Vulcanization

The chemistry of vulcanization is probably that phase of rubber chemistry which has attracted the most attention during recent years. One of the earliest of the various processes of vulcanization, other than the previously mentioned hot vulcanization with sulfur, is the so-called "cold" process, discovered by Alexander Parkes in 1846. He vulcanized sheeted crude rubber by dipping it for a few minutes in a 1 per cent solution of sulfur monochloride, S_2Cl_2. This is conceived to be a direct chemical addition up to a limiting composition of $C_{10}H_{16}.S_2Cl_2$. This result, however, yields a solid, usually obtained as a powder. When quantities under 3 per cent are added we obtain soft, vulcanized rubber, as known in the form of toy balloons, nipples, and surgeons' gloves.

THE PEACHEY PROCESS—A most interesting cold process has recently been developed by the Englishman, Peachey, who first proposed his new plan in 1918. This new process consists in exposing rubber alone, or a mixture containing any useful pigment, to two gases alternately, namely, sulfur dioxide and hydrogen sulfide. The first diffuses into the rubber until the proper quantity has been taken up and then the second gas is permitted to diffuse in it. They interact with the liberation of nascent sulfur, bringing about a rapid vulcanization without the aid of heat. The claims made for the process consist essentially in the advantage given to rubber compositions which would otherwise be injured if the usual hot vulcanization method is employed. Mixtures containing leather, cotton fiber, and colors which would be altered by heat, particularly with respect to rubber surface clothing, may now be vulcanized at ordinary temperatures without injury. The process has not yet been conducted on a large production scale.

NITRO COMPOUNDS—Somewhat earlier, in 1915, the Russian, Ostromuislenskii, discovered that a hardening similar to vulcanization occurred when rubber is heated without sulfur in the presence of certain nitro compounds or peroxides, such as trinitrobenzene or benzoyl peroxide. Whether this is a gelation phenomenon, an adsorption, or an additive chemical reaction has as yet not been proved.

HOT VULCANIZATION—We now come to a discussion of what has been learned regarding the hot vulcanization of rubber with sulfur, which is the only process in large commercial use. The idea prevalent fifteen years ago when I first entered the rubber industry, and one which still prevails in the minds of many practical men, is that sulfur vulcanization does not occur until the temperature of the mixture has reached or exceeded the melting point of sulfur. Vulcanization to-day, however, is known to occur at ordinary temperatures if the time be long enough—sixty to ninety days in the case of old-fashioned mixtures. When certain recently discovered powerful catalysts are employed in the mixture, the hardening may take place on standing over night. Whether the temperature be low or high, we know that the amount of sulfur that enters into combination with rubber increases with time and rise of temperature; that is, the velocity of the reaction is proportional to the time at constant temperature and if the temperature and the time be fixed, the amount of sulfur entering into the molecule is dependent upon the quantity originally present.

When small amounts of, say, 3 per cent of sulfur are thus "combined," as we say, there results the soft rubber of commerce. In almost all instances there is a slight excess of sulfur left in solution in the rubber as "free" sulfur. This usually gradually diffuses to the surface, where it crystallizes out and appears as a powder or "bloom." This amount of combined sulfur, expressed as a percentage figure in terms of rubber as 100 per cent, is known as the "coefficient of vulcanization." No chemical individual of the rubber hydrocarbon and sulfur has been isolated from soft, vulcanized rubber mixtures. Yet their properties vary from the under-vulcanized, or "under-cured," mixtures in which the amount of combined sulfur is low, to the over-vulcanized, or "over-cured," mixtures in which the amount is high.

There are wide and, to the manufacturer and consumer, vitally important differences in physical properties, between under-, proper, and over-cured rubber articles. Yet we have as yet only theories of a general character to explain the nature of the product of vulcanization.

When a large excess of sulfur is used in a mixture, addition goes on up to a maximum of 32 per cent of combined sulfur, and there results the only compound which has been isolated—a monosulfide, C_5H_8S, or, as usually written, $C_{10}H_{16}S_2$. It is in the laboratory a brown, dry powder. In the factory and in commerce we know it as hard rubber or ebonite, in battery jars, sheets, fountain pens, and so on.

Ostwald's theory of physical change led to the many discussions that have arisen between the two camps of chemists: those who expound the sulfur adsorption theory of Ostwald and those who stand by a chemical theory. The great father of rubber chemistry, Weber, was an exponent of the chemical theory. We to-day, I believe, adhere to a combination of a chemical and physical theory as most reasonable for the explanation of vulcanization. The fact that no compounds have yet been isolated in the soft rubber range of vulcanization is no reason for us to believe that a purely physical theory alone will account for it.

We have not yet found a process by which the combined sulfur can be removed and the original rubber regenerated. The rubber industry is, however, economical, and uses up its waste products. The old tires, shoes, and hose are gathered and reclaimed by processes which simply hydrolyze and separate the cotton while the vulcanized rubber is softened to permit it to be plastic enough for remixing. Let me here state in justice to my brethren in the industry, all statements to the contrary notwithstanding, that reclaimed rubber is a valuable ingredient in many rubber mixtures. Over 70,000,000 pounds are used annually in this country, or about one-quarter of the amount of crude rubber employed; an economic consumption of no mean magnitude, of what otherwise would be waste.

ACCELERATORS

While the nature of the product obtained when sulfur and rubber interacts is indefinite, the rubber chemists in recent years have reached some pretty clear conceptions of the mechanism of the process, particularly the part played by catalysts. From the day when Goodyear used white lead, various types of inorganic compounds have been employed as accelerators. They have been chiefly lead compounds and oxides of the alkaline earths, with, in laboratory experimentation, for instance, the hydroxides of the alkali metals and the sulfides, and hydrosulfides of the alkalies and alkaline earths.

The use of organic compounds for speeding the time of vulcanization is probably one of the most important developments in the chemistry of rubber and of greatest value in practical affairs. They have served not only to increase the rapidity of turn-over in the factories, but have led to increased physical properties of rubber mixtures. The name of the first person to use organic accelerators in rubber factory practice has never been published. The writer feels it to be in the interests of truth to give here public credit to the two pioneers of the organic accelerator. The laboratory record books of The Diamond Rubber Company, which was later consolidated with The B. F. Goodrich Company, show that Mr. George Oenslager, in the early months of 1906, experimented with aniline oil, and a long list of other organic compounds, with the definite purpose of hastening the time of vulcanization. In June of that year, Mr. A. H. Marks directed its use in factory formulas, and in February 1907 he used thiocarbanilide. The German patents were not published in this country until 1912, so that it may be safely stated, unless some one comes forward with earlier unpublished data, that the use of the organic catalysts of vulcanization originated with Mr. Oenslager and Mr. Marks in 1906.

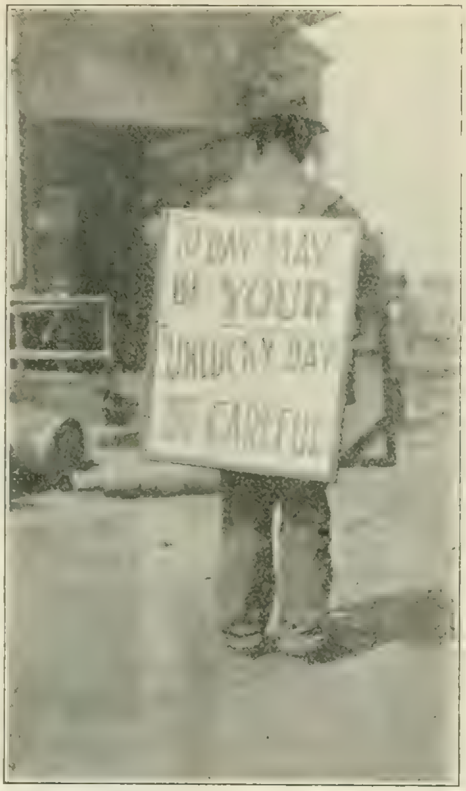
Basic compounds were first used, particularly nitrogen derivatives. The literature mentions large numbers of them; piperidine, aldehyde ammonia, hexamethylenetetramine, the aliphatic amines, and so on, have been used in practice. The dithiocarbamates came into published literature with Ostromuislenskii in 1915. Bruni, Maximoff, and others have studied the thiuram disulfides, and within the last few years the xanthates, particularly the zinc salts, have been discussed. In rubber mixtures, for laboratory purposes, accelerators have been found which permit the vulcanization of rubber and sulfur at all ordinary temperatures. Mixtures can now be made which will vulcanize over night on standing at room temperatures and at very short times from then on up to usual factory practice, which are temperatures under 150° C. By proper selection of accelerators, even cements may be vulcanized to gels on standing for several hours at room temperatures.

How these substances act and why, have been pretty well established. Zinc oxide in a mixture has long been known to promote the action of the accelerators. Kratz, Flower and Shapiro stated that zinc salts are formed in many instances, and that these are the active accelerators. They show how the thioureas can form zinc salts through tautomeric change. These are similar to the zinc dithiocarbamates. Bruni and Romani assume that the thiourea is converted into a zinc salt, as just mentioned, and that sulfur acting with this zinc salt forms a thiuram disulfide which acts as a vulcanizing agent. Twiss studied allotropic forms of sulfur but was able to show no difference in the action of the two.

In my opinion, however, the best work on the theory of acceleration has been that of Bedford and his associates, Sebrell and Scott. They show hydrogen sulfide to be an important factor in the mechanism of vulcanization and, generally speaking, that all vulcanizing reactions may be ascribed to some form of polysulfide sulfur. The original accelerator then, whether metallic, organo-metallic, or organic, forms with sulfur polysulfides which yield sulfur in a more active state than when in its elementary form.

These substances cannot be termed catalysts in the true sense, at least so far as our idea of contact catalysis is concerned. They do serve to permit sulfur to be more actively taken up by rubber, but in doing this they are often changed themselves and then are left permanently changed in the mixture. Intermediate compounds are formed. The reaction is more chemical than physical. There is no poisoning of the accelerator except the retarding action of acids. Nor is it a case where a given quantity may react with a relatively large amount of the reacting substances. The quantity of accelerator has a very definite relation to the time and degree of vulcanization. Furthermore, essentially all accelerators, according to the best of our evidence, such for instance as that of Whitby and Walker, show not only an increased speed of reaction but also an increase in the tensile properties of the rubber. We gain, therefore, two points: one, the velocity of reaction, and the other, improved physical properties. We had better call them accelerators and let it go at that.

The physical properties of rubber mixtures have been studied, and chemists are more and more coming to use the stress-strain relations as guides to the evaluation of mixtures. Wiegand, in a most interesting study, showed that the addition of different volumes of different dry inorganic powders which we call pigments increased the energy-absorbing capacity remarkably in the case of gas-black, lampblack, and zinc oxide; increased it to a slight degree in the case of a fine clay, but decreased it in the case of whiting, fossil flour, barytes, and glue. He also called attention to what the older rubber men have long known, that the tensile strength of a rubber mixture usually computed against the cross section when at rest and before testing may, if computed against the section at the break, exceed twenty tons per square inch, which would bring rubber into the class of mild steel. It is the only substance for which the elastic limit extends to the point of rupture. The number of foot-pounds of energy that can be stored in a unit weight of the material exceeds steel many times. It is an interesting physical study which tells us that such stored energy in tempered spring steel is only 95.3 foot-pounds, while in a high-grade rubber it is over 15,000 foot-pounds.



"Safety First" at Tennessee Coal, Iron & Railroad Company Plant

To explain the properties given to rubber mixtures by these dry powders, determinations have been made of the particle size, by Green and others, who have photographed under the microscope these various materials. From these and other data we come to one important conclusion, namely, that the particles of large size are not as strength-giving in rubber mixings as those of small, while particles which seem to separate from the rubber when stretched are the ones which are of less value in mixings which must resist abrasion.

The use of carbon black and zinc oxide is really based primarily not only on their fineness of subdivision, but on some factor which we have yet to determine but which may be due to an increase in the interfacial tension. That is, they are so fine in subdivision and so specific in their adhesion to rubber that they not only approximate what we may term "mass molecules" but have a degree of specific adhesion to the rubber, making it thereby difficult to break them loose when rubber is submitted to stress. There has been an amusing controversy between the exponents of the sale of carbon black and zinc oxide over which one is the best. I will leave it with you; they are the two best materials—one is the king and the other the queen of pigments. You may use them singly or together and take your choice as to which will have the preference in the processions of your royal family. Some unpublished data go to show, however, that both are essential to the highest values in some rubber mixtures.

You must not now let me leave you with the idea that these few substances constitute the whole of rubber mixtures. I wish they did, for then my early dream would approach realization. When I first came into the rubber industry fresh from a university I thought how easy it would be for me in a relatively short time to solve this compounding problem. I had been trained in the phase rule, with a reasonable amount of mass law and electrolytic dissociation thrown in for good measure, so I hoped, of course, to find rubber a simple three-component system capable of explanation on a triangular diagram. But as soon as I became acquainted with the properties in compounding of from 400 to 1500 dry pigments and with organic accelerators which in the years that have followed have run upwards of a thousand; with reclaimed rubber of a hundred grades; with crude rubber in twenty to a hundred different kinds, and all these to be used in mixtures with cotton fabric of thousands of weaves to make ten or twelve thousand different articles in different sizes, shapes, and for different purposes, I came to have a very high respect for the practical man. After all, rubber, as the consumer gets it, is not a simple mixture of rubber, sulfur, and accelerator; in the interests of numerous physical properties required for service in the form of shoes, frictions, treads, and belt covers, other materials must be used. We have found in recent years how these materials serve practical purposes and are not simply to be considered as cheapening fillers. In point of fact, to-day many pigments cost more than crude rubber. The colloid particle, the fumed products, and the ground inerts all have definite uses in giving us serviceable as well as economical rubber products. The rule-of-thumb methods are gone from the leading laboratories, but the variables are so extended that the service test has become the final judge of the value of any mixture.

May I be pardoned if I speak from the vantage of research and experience to those who would write specifications for rubber articles? For years plantation grown crude rubber was ruled out—organic accelerators and carbon black excluded. Yet the industry advanced, used these substances, and improved the quality of its products. Where specifications seem essential, may I recommend only tests, and those which have a definite relation to the service the article is to render?

While we have developed research laboratories to show us why, development departments to show us how, testing machinery to give us results, we, nevertheless, are constantly faced with the question: Will it age? Rubber is a perishable product. For any purpose a knowledge of the rate of deterioration is most advantageous. This is a serious problem and a vital one to manufacturer and consumer. Heat, light, oxygen, and sulfur play their parts in the drama but as yet no definite theory to account for the varied rate of aging has been proposed. In the vast majority of cases too rapid decay is due to over-cure of the mixture. To determine over-cure and how rapidly a new compound will age in comparison with one of known properties, I devised a test some ten years ago by which the rate of decay could be predicted. I have recently published some results from this ten years' experience from which I now believe that in the heat of 70° C. with plenty of air, one day in the "short life oven" corresponds to about six months of natural aging. I do not hesitate to recommend to my friends in the rubber industry more attention to this vital problem.

As not only a chemist but a practical rubber man, I could not let go this opportunity of saying something of the future of rubber. The automobile has made the rubber industry, just as the rubber industry has made the automobile. You could not enjoy your cars if you had to follow the practice of Germany during the war, with steel springs and wooden blocks and other devices which were used in the attempt to get along without the softness and springiness of the rubber tire. Improved highways, whether for train or motor car, are essential to human prosperity and growth. It is rubber in the form of tires, air brake hose, insulation, packing, and manifold others which has made these highways capable of efficient and comfortable use.

With about twelve million automobiles in the world and about ten million of them in the United States, one must look forward and let his mind revert from days of depression to the future of larger use of these articles. There are about twenty-four million homes in this country; there is scarcely a new house built nowadays without its garage. When one looks at the map of the world and considers the millions of people who will need improved highways for transportation purposes throughout the great continents of Asia and Africa, let alone an increasing desire for these facilities in Europe and America, we can expect a vast increase in motor car transportation and with it of rubber tires.

Rubber articles have woven their way into myriads of uses. We have found, for example, that soles and heels of rubber give comfort and yield long resistance to wear, for rubber mixtures outwear leather wherever they have been placed in comparison with it. The home, the shop, the school, the office, directly or indirectly, derive benefits from them. It is one of those substances which unfolds possibilities for new applications which stagger the imagination. The chemist has and will continue to play a most vital part in these developments. The automobile tire of ten years ago gave a satisfactory mileage of four thousand miles, while to-day the cord tire would scarcely be considered of value on your cars if it did not give you ten or more thousand miles. Essentially all rubber articles have been improved in service, achievements due in no small part to the developments in the chemistry of rubber of which I have spoken.

With this picture in mind, one can see only larger values, provided, I believe, that the chemists of this industry are supported by the financiers in the conduct of research work. Many problems are still unsolved; civilization changes; only as an industry bases its progress year by year upon the results of research, will it attain permanence in its growth.

Some Research Problems of the Canning Industry

By W. D. Bigelow

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In any branch of industrial research, problems must be studied which at first appear to have slight connection with the industry concerned. It is often necessary to investigate the character and methods of producing the raw materials. A study must be made of the purposes for which the finished products will be used, and the storage conditions to which they will be subjected.

The canning industry is no exception in this respect. The success of the industry depends first of all on the satisfaction and success of the growers who raise the raw products. The uniform quality of seed supplies is of fundamental importance. Serious consequences sometimes result from seed of low germinating power or of a different variety from that specified. The distribution of seed contaminated with fungus diseases is certain to cause disaster. The canner generally distributes seeds to his growers, directs them with respect to the time of harvesting, and in many ways is held responsible for the crops produced. He is therefore interested in a wide range of agricultural problems.

Again, after the food is manufactured and sold many questions arise regarding its transportation and storage. When shipped in the winter there is danger of freezing, which damages the appearance of some products. The amount of damage probably depends on several factors, including the extent of freezing, whether the product was stationary or being transported while freezing and thawing, and the time occupied in thawing. No systematic study has been made of the influence of freezing on the appearance and quality of canned foods.

Food Poisons

Questions sometimes arise regarding the wholesomeness of foods which have been consumed. Any sudden attack of illness involving abdominal distress is likely to be construed by consumers and sometimes by physicians as evidence of food poisoning, and some article of food recently consumed, and which the patient is not accustomed to eating, is sometimes designated as the probable cause of the illness. Thus it is important that our knowledge of the general subject of food poisoning be greatly extended.

The study of food poisoning is one that pertains peculiarly to public health, and it involves all classes of foods. There is no type of food poisoning that is peculiar to canned foods.

During the last generation our ideas of the character and cause of food poisoning have undergone a fundamental change. A generation ago a type of illness characterized by purging, vomiting, and great intestinal pain was known as ptomaine poisoning, and was believed to be caused by chemical products due to the splitting of the protein molecule by bacteria of unknown nature. Something more than twenty years ago it was shown in Europe that illness of this type was caused by a group of microörganisms known as the Gaertner bacteria, of which the paratyphoid bacterium is a type.

In recent years Rosenau and his associates, after an exhaustive study of the subject, have concluded that the term "ptomaine" is entirely a misnomer, and have been unable to find any evidence of the existence of decomposition products produced in food by bacteria which are poisonous when taken by mouth. It is now recognized, therefore, that the so-called ptomaine poisoning is caused entirely by infection and can be prevented by the ordinary precautions demanded for the prevention of infection. Bacteria of this class are not spore formers and hence do not survive the heat of processing canned foods.

During the last few years the *B. botulinus*, long known in Continental Europe, has been found in this country and has caused a number of cases of illness and death. This is the only spore-bearing organism which produces substances that are poisonous when taken by mouth. Although the growth of this organism is not limited to canned foods, and although it has been encountered more commonly in home canned products than those packed commercially, it has remained for the canning industry to finance the investigation of the subject that has been made in this country. This work has been conducted by the Harvard Medical School in the eastern states and by the medical departments of the University of California and Stanford University on the Pacific Coast with the coöperation of the U. S. Public Health Service. A comprehensive monograph will soon be published describing the outbreaks of botulism in this country, and treating of the occurrence of *B. botulinus* in nature.

Nutritive Value of Foods

Until recently the nutritive value of foods was thought to be measured by their content of protein, carbohydrates, fat, and mineral constituents. In this respect canned foods cannot be differentiated from the same foods stored in the raw state. Since the important role of vitamins in foods is now unquestionable, their consideration with reference to canned foods raises many questions which have not been answered.

The early workers on this subject stated that certain foods lost their vitamins when heated to a temperature of 120° C. and that canned foods were deficient in vitamins. The more recent work does not confirm this. It is now believed that the amount of vitamins A and B is only slightly reduced by the heat of processing canned foods; and that the antiscorbutic vitamin is more sensitive to heat but may be as sensitive to oxidation as to heat. Therefore it seems probable that ordinary cooking in an open kettle may be as destructive of the latter as the processing of canned foods. This can only be conclusively determined by dividing a single lot of a raw product into two portions, cooking one in an open kettle and exposing the other to the canning process and then determining the vitamin content of each.

We know little about the influence or variety of conditions of storage upon the vitamin content of our raw fruits and vegetables. It has been shown that milk varies enormously in its vitamin content because of the varying food given the cow. Some vegetables lose their vitamins gradually when stored in the raw state. Hence it is important that a broad study be made of the vitamin content of all of our foods, not only when freshly harvested but also under all conditions of production and storage, both of the raw product and of the manufactured food.

As a single illustration, if we wish to consider the vitamin content of tomatoes, we are confronted by the effect of variety, locality, soil fertility, degree of ripeness and, closely related to it, ripening off the vine as is customary with tomatoes shipped north in the winter season, home cooking, canning, drying and subsequent storage. With other vegetables these and additional questions must be considered in a like manner.

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We know that after three years of storage canned tomatoes are almost, and possibly entirely, as rich in the least stable of the vitamins as when first canned. Little has been done to determine the amount of deterioration of the vitamin content of raw products during storage, but in a few cases this has been shown to be considerable. This question therefore suggests itself: May vitamins be preserved better by storing the raw product or by canning it before storage? The data now available do not enable us to answer this question.

Processing Studies

The operation known as processing (sterilizing) canned foods was developed by the cut-and-try method. Samples of the foods in cans of various sizes were heated at different temperatures and for different times and the cans held in storage to determine whether spoilage would occur. A temperature and time of sterilization which was found to be sufficient to keep the food, and which yielded a product of acceptable appearance and flavor, were adopted as satisfactory and used in canning the product. If it developed later that more or less spoilage occurred, the temperature or time was increased. Only in recent years has it been fully appreciated that the processing of canned foods is a complicated operation and the study of its fundamental principles undertaken.

Bacteriological studies—The characteristic feature of the canning operation is the destruction of the bacteria by means of heat. Therefore it is of the first importance to know the time and temperature of the process necessary with each food to destroy the most resistant bacteria. When this question was taken up three years ago we found that no methods were available for determining the thermal death point of bacteria at temperatures above the boiling point of water. The first step, therefore, was the development of such a method. The bacteria causing the spoilage of a considerable number of canned foods were then isolated and their thermal death point determined. Those that were found to be the most resistant to heat were subjected to an intensive study at various temperatures, in the juices of typical foods, as well as in phosphate solutions of different hydrogen-ion concentration. The work should be extended to non-spore-bearing bacteria at temperatures below the boiling point of water, as well as to yeasts and molds, in order that we may have information regarding the sterilization of acid products, such as fruits and tomatoes, that is comparable to the information now available regarding foods of lower acidity.

The time and temperature necessary for sterilization are profoundly influenced by the number of bacteria present. It is therefore important to know the conditions which tend to increase the number of bacteria in the raw product. We should know the sources of resistant bacteria, and with this in view studies should be made of the raw product, of all portions of the canning plant, and of the water supply. A beginning has been made on these studies, but much remains to be done.

Heat penetration studies—A complete knowledge of thermal death points would be of no practical value to the industry without an understanding of heat penetration. The transfer of heat to the center of the can depends on several factors, including the nature and consistency of the food. When a batch of cans is placed in the retort the outer portion of the contents of each can heats rapidly, but the penetration of heat to the center of the cans is sometimes greatly delayed. In processing canned foods it is obviously necessary that all portions of the can be heated sufficiently to effect sterilization. In order to apply the thermal death point of resistant organisms mentioned above to the sterilization of canned foods we must therefore know the temperature of the center of the can during the entire period of processing.

The temperature of boiling water or even 80° C. (176° F.) is sufficient to sterilize if continued long enough. The time required would be so great, however, as to make sterilization at low temperatures impracticable. For instance, a process of eighty minutes at 121° C. (250° F.) is sufficient to sterilize No. 2 cans of corn containing the more resistant thermophilic bacteria. At the temperature of boiling water, twenty-five hours would be required to give a process of the same sterilizing efficiency.

In order to understand the sterilizing value of a certain time and temperature of process, therefore, we must have the heat curve of the center of the can throughout its period of heating. It is also necessary to understand thoroughly the heat distribution of different types of pressure kettles employed.

This work was made more difficult by the fact that canned foods are sterilized after the cans are sealed, and it is still further complicated by the continuous cookers now employed with many products in which the cans rotate while passing through the sterilizer. In undertaking the work it was necessary to develop pyrometers which could be used in determining the temperature of a sealed can when enclosed in a sealed retort, and if necessary while the can was rotating and being heated at any desired temperature and while it was located in any desired portion of the sterilizer.

In this way heat penetration curves have been established for many kinds of canned foods packed in different ways and processed under different conditions. These curves are of little value by themselves. Considered, however, in connection with the thermal death points of resistant bacteria and with the acidity of canned foods during the period of processing they are of value in the fundamental study of the subject.

Material progress has been made in the study of heat penetration, but much remains to be done.

Acidity of canned foods—A third factor in processing is the acidity of foods. The heat-resistant, spore-forming bacteria will not grow in foods as acid as tomatoes or the ordinary fruits. Moreover, all bacteria are killed in acid fruits and tomatoes by heating for a short time in boiling water. On the other hand, foods of low acidity, like the ordinary vegetables, can be safely processed only at higher temperatures in pressure cookers.

The acidity (hydrogen-ion concentration) of the juices of the majority of canned foods has been determined. The data thus obtained are of value in establishing the process necessary for sterilization. The acidity of the juices of canned foods, however, varies somewhat from that of the liquor of the food during sterilization. With foods that are well buffered, the acidity increases during processing because of the influence of heat. With foods that are not well buffered, such as fruits and some root vegetables, the acidity of the liquor of the can is not appreciably changed by heat, but increases owing to the diffusion of the juices into the liquor surrounding the solid pieces of fruit. In nearly all canned foods, therefore, the acidity of the free liquor increases during processing, and we should have full information regarding the acidity of the liquors of canned foods during the processing period.

This question has been studied in the laboratory with reference to a number of typical foods. The work should be greatly extended and as far as possible carried into the field and studied under commercial canning conditions.

STERILIZATION OF CANNED FOODS—By combining the curves representing thermal death point and heat penetration, taking into consideration the time required for heating the retort to the temperature desired for sterilization, it is possible to calculate the time and temperature which should be necessary theoretically to sterilize a certain food when contaminated by a certain bacterium, the sterilization being accomplished under prescribed conditions.

Such calculations are now being made and make possible a critical study of the processes now used in the industry. They show the importance from the standpoint of sterilization of technological details which are not usually considered to have sterilizing value. For instance, the initial temperature of the center of the can; the length or character of the exhaust; the heating of the retort (when not already hot) before filling it with the food to be sterilized; the accuracy of the retort thermometer; all influence the time and temperature of process necessary to effect sterilization, and an approximately quantitative statement regarding the influence of each may now be made.

The value of such theoretical processes, however, lies chiefly in the fact that they make practicable an intensive study of sterilization that would otherwise be almost impossible because of the amount of work involved. Such a study can best be made by inoculating cans of various foods with a definite number of bacterial spores of known resistance to heat and determining the time and temperature of heating under commercial canning conditions necessary for their destruction. The theoretical process time mentioned above serves as a guide in processing inoculated cans, and greatly reduces the amount of experimental work necessary to determine the proper process.

Several such experimental packs with inoculated cans have been put up, and the results confirm the value of the calculated process times mentioned above and show the practicability of combining the two methods of procedure.

This work should be greatly extended. Experimental packs with inoculated cans should be put up with foods of different kinds in different sections of the country. In one pea-growing region a process of thirty-five to forty minutes at 116° C. (240° F.) is believed to be required to sterilize peas, while in another from twenty to twenty-two minutes are believed to be sufficient. In some corn districts it is recognized by canners that a process of from seventy-five to eighty minutes at 121° C. (250° F.) is required to sterilize corn, while in other localities it is held that a shorter process is sufficient. In each case the hydrogen-ion concentration of the product of the two localities is substantially the same and there is no apparent reason from the nature of the product why they should not require the same process.

In one case where this question has been studied by means of inoculated cans, it was found that the shorter process for peas mentioned above did not kill the resistant bacteria which had been found to cause spoilage in other localities. The process employed in that district, therefore, was not sufficient to insure sterilization. The bacterium with which our experimental cans were inoculated is widely distributed, and may be expected at any time on the peas of the locality in which this work was done. When it appears, spoilage is likely to occur.

The bacteria referred to in this connection are nonpathogenic and are far more resistant to heat than any pathogenic bacteria. There is therefore no question of public health involved, but the amount of spoilage caused by bacteria of this type is sometimes considerable, and is recognized as a matter of importance in the industry.

PREHEATING AND EXHAUST

With almost all products the cans are sealed hot in order that after processing and cooling a partial vacuum will remain. Some products are preheated and filled into the can hot. Others are filled cold and a hot brine or sirup added. Still others are "exhausted," that is, they are passed through a steam box or hot water bath after filling and before sealing.

During recent years it has been learned that some form of preheating is important with many products for other reasons than securing a partial vacuum. With some products of slow heat penetration the temperature of the center of the can does not reach retort temperature during the entire period of processing. In such cases the sterilizing value of the process is greatly increased by having a high initial temperature.

Some fruits have a considerable amount of air in their intercellular spaces, and if canned in that condition the oxygen accelerates corrosion and increases the perforation of the cans. The presence of an undue amount of oxygen within the can causes discoloration with some products and with others produces an undesirable flavor.

The information thus far available on this subject is of a general nature and rather superficial. Much yet remains to be done. A study should be made of the gas content of various fruits and vegetables while in the fresh state and under different methods of storing. A study should also be made of the influence on the gas content of exhausting by different methods and under different conditions. The relative merits of steam and hot water exhaust are only partially understood. The relative merits of exhausting at different temperatures and for different lengths of time should receive more attention.

DISCOLORATION OF CANNED FOODS

It sometimes happens that canned foods or the cans containing them develop some type of discoloration, either during processing or during subsequent storage.

When foods of high protein content are heated a trace of hydrogen sulfide is liberated, which gives rise to several forms of discoloration in canned foods. With some varieties of beans hydrogen sulfide combines with the tin and forms a more or less dark discoloration over the entire inner surface of the can, except that bordering on the air space at the top of the can.

With other products the hydrogen sulfide liberated from the protein by the heat of processing passes into the air space and combines with the iron in the top of the can, forming black pulverulent patches which may either adhere to the plate or be rubbed off into the contents of the can. Such discolored patches are found most commonly in canned corn, but are also found in lobster, shrimp, and some varieties of fish. The cans used with shell-fish are sometimes lined with a parchment paper and in that way the discoloration mentioned is partially controlled.

With corn it has been found that the presence of air greatly increases the amount of discoloration formed and that every possible precaution should be taken to insure the tight sealing of the can. The presence of eight or ten milligrams of zinc coated on the top of the can has been found to reduce greatly the amount of iron sulfide discoloration produced in experimental packs.

The amount of this discoloration experienced by corn canners is still a source of annoyance, and any progress that may be made in overcoming it will be of value to the industry.

It has recently been determined that the black discoloration in canned sweet potatoes is due to the oxidation of the iron of the can and its subsequent reaction with some substance resembling polyphenols which occurs localized in the potatoes. This discoloration may therefore be entirely eliminated by properly filling, exhausting, and sealing the cans.

Black hominy has long been a source of great annoyance to packers of that product. It is due in part to the low hydrogen-ion concentration produced by lying the corn to remove the hull. A method has recently been suggested for controlling this difficulty at least in part, by shortening the lying period and completing the dehulling by mechanical means. This method has been developed on a laboratory scale but has not been tried on a commercial scale, and should receive further study.

A pink discoloration is sometimes found with certain canned fruits, as for instance with peaches and pears. This is sometimes the result of excessive sterilization but may be connected with the variety of fruit, the degree of ripeness, and possibly with the location in which the fruit is grown. Discoloration of this type is infrequent and is imperfectly understood.

INFLUENCE OF HARD WATER

It is known that hard water, when used for blanching peas or beans or for the preparation of brine added to the cans, increases the toughness of the canned product. This influence is apparent immediately after canning but becomes more pronounced with storage.

Thus far only preliminary work on this subject has been done. We know little about the influence of waters of medium hardness on the toughness of canned legumes, and except in the case of waters that are distinctly hard we cannot determine by the analysis of water whether or not it will be advantageous to instal a softening process.

TIN PLATE

During the last ten years a systematic study has been made to determine the character of the tin plate best adapted to packers' cans. This question is exceedingly complex and difficult.

No methods have been developed by which plate may be examined in the laboratory and its suitability for the manufacture of cans determined. The only method of testing the service value of the plate is to manufacture it into cans and to pack food in the cans and study both containers and contents at intervals during protracted storage.

The influence of variations in the method of constructing the can, as well as of storage conditions, and the varying action of different kinds of foods add to the complications and make the study almost infinitely complex.

MANUFACTURE OF STEEL BASE—The steel used for the manufacture of tin plate should be as free as possible from segregation and sufficiently soft so that the plate can be sent or rolled without cracking. It is believed by steel manufacturers that tin plate should be made from steel having the following average composition:

Carbon less than 0.2 per cent
Sulfur less than 0.05 per cent
Silicon less than 0.025 per cent
Phosphorus from 0.05 to 0.1 per cent

It is not known whether a materially better quality of plate would result from the manufacture of steel containing any of these constituents in smaller amount. Further work is needed in studying the influence of variations of the constituents mentioned above on the service value of the can.

We do not know whether a heat of steel which is brought to the desired composition quickly and with a minimum amount of "working" gives better results when manufactured into tin plate than a heat which has been badly made and which is brought to the proper composition only after repeated furnace additions.

Both Bessemer and open-hearth steel are used for making plate. The Bessemer steel is ordinarily used only for making the can bodies, while the open-hearth steel is usually employed for the ends, which are subjected to bending strains and require a higher degree of flexibility than is necessary for the bodies.

Better results seem to come from steel annealed at temperatures of from 1200° to 1400° F. than when the annealing is done at higher temperatures, but information on this subject is fragmentary.

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The steel is usually first rolled out in the blooming mill, where it is worked all directions until a bloom five or six inches square is made. The bloom is then rolled down into sheet bar. In some mills, however, the ingot is rolled directly into sheet bar, and in this procedure is not turned and rolled on all sides as in the blooming mill. The influence on the service value of the can of these variations in methods of rolling has not been studied.

It is well known that with heavy cold rolling a sheet can be produced of so hard and smooth a finish that the same weight of tin appears to give it a heavier coating after tinning than one cold rolled to a less extent. Whether the coating adheres to the plate as well, and whether the resulting plate gives as good service in cans as when softer cold rolling is practiced has not been determined.

COATING OF BLACK PLATE—During the last generation there has been a great change in the methods employed in making tin plate. We are not familiar with the methods employed in Wales forty or fifty years ago, but we know in a general way that after the black sheet was pickled and washed it was heated in an oil bath for some minutes before being introduced into the tin pot. After being dipped into molten tin it was heated again in an oil so that the excess tin might drip from the plate.

According to the present practice the plate after pickling is held in a bosh of water slightly acidified with acid until it is taken to the tin pot. The tin pot contains a partition reaching from the top of the pot to a point below the surface of the molten tin. On one side of the partition the tin is covered with zinc chloride and on the other side with palm oil. The black plate passes into the molten tin through the layer of fused zinc chloride, goes under the partition mentioned above and passes out through the layer of palm oil. In this way it reaches the molten tin without previous heating, is only in momentary contact with the tin, and leaves the pot while still hot.

The black plate is more or less porous, and during the pickling operation these pores probably become filled with hydrogen gas. Under some conditions, which are only partially understood, it is believed that this gas may interfere with the perfect coating of the plate, in some cases causing blisters.

A study of modifications of the methods of tinning and their influence on the service value of the cans should be made. It is conceivable that if the plate were heated before being introduced into the tin pot, as was the practice in the oil baths formerly used in Wales, the gas might be eliminated from the pores of the black plate to such an extent as to increase the service value of the latter when made into cans. Moreover, it is possible that such heating might so improve the surface of the black plate that a more continuous coating would be secured.

The amount of tin on the grade of plate used in the majority of packers' cans is probably not sufficient to permit the tin to flow and increase the continuity of the coating if heated in an oil bath after tinning. Still some experimental work on this subject should be undertaken, studying the influence of heating for a number of minutes after coating on the service value of cans made from the plate.

After the plate leaves the tin pot the palm oil adhering to it is removed by means of bran or some other absorbent material. Sometimes peanut shells are used, and since they always contain some sand the plate cleaned with them is scratched. These scratches greatly increase the susceptibility of the plate to rust, and are readily apparent whenever a sheet of plate begins to rust.

It has been determined that the weight of coating has a profound influence on the action of fruit acids in perforating tin cans. Heavily coated tin plate resists perforations longer than plate of ligher coating. This fact suggests the advisability of a study to determine whether plate cleaned with peanut shells, and hence covered with scratches, is more susceptible to perforations than plate cleaned with bran

ENAMELED CANS—Red fruits are more or less bleached when packed in ordinary cans. For this reason it has become customary to enamel the inside of cans intended for packing red fruits. Such enameled cans protect the color of the fruits, but are much more susceptible to perforation than plain cans. The reason for this is not understood. Walker has suggested that it may be due to depolarization by the unsaturated carbon bonds of the oil used in the manufacture of the so-called enamel. This question should be studied further. A coating is described which will protect the color of the red fruits and will lessen rather than increase the susceptibility of the plate to perforation.

PERFORATIONS—When canned fruits are stored, the fruit acids attack the tin plate to a greater or less extent. Sometimes the corrosion is general, attacking the entire surface of the can to an apparently equal extent. At other times the corrosion seems to be localized and results in holes being eaten through the plate in a relatively short time.

As has been already stated, some products which do not perforate plain cans give serious trouble when packed in enameled cans. During recent years we have made progress in the study of perforations, but much yet remains to be done. The amount of oxygen in the can has a profound influence on the formation of perforations. When cans are loosely sealed, so as to permit the entrance of air, perforation occurs quickly. With some products a beneficial effect is produced by removing a portion of the air by means of preheating.

There are other factors involved, however, than the character of the tin plate, the amount of air present, or the kind and amount of acid in the fruit. What these factors are remains to be determined.

The Pioneer's Field in Petroleum Research

By Van H. Manning

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IN order that the picture which I wish to present to you may be adequately visualized we must concede that from the time of the first commercial "discovery" of oil in the United States the resultant industry has been one of continuous expansion and the pioneers of this industry have set a beacon of order and efficiency which lights the highway to progress; a superphase with invaluable applications to the problems of humanity in this great industrial age. These pioneers have been engaged in a contest of discovery and invention which has meant systematized methods in production and in the development of processes of utilization. Looking backward, we can say of these American pioneers that their spirit of adventure into the unknown caverns of the earth and through the uncharted seas of science has within the short space of a few years brought about incalculable and beneficial advancement to the peoples of the world. With this record before us we now turn to the realm of the future, a future accentuated by a universal demand for greater efficiency and economy in the production and utilization of a wasting asset. I am not so bold as to prophesy the future, but I do assert that we have not reached the goal of scientific effort in developing to their fullest degree the petroleum resources below and above the ground—and as the subject of my address implies a field in petroleum research, I revert to the reports which I have made to the Board of Directors of the American Petroleum Institute since August 1919, on the subject of "Improvements in Methods." In these reports there was outlined in a general way a plan for the conduct of the work which should be fostered by the Institute. This work comprehended the technical field of petroleum and natural gas. As a general rule, governmental and state agencies, research foundations, industrial laboratories, and educational institutions have been making their investigations and researches independently. I make no attempt to analyze the character of the work of these organizations except to say that they have accomplished work of the very highest quality and the present technic in the petroleum industry is the outgrowth of these many agencies; however, many of the results obtained have been at the expense of much unnecessary duplication of effort and financial loss. It is realized that there is some research work subjected to limitation of secrecy or a dominant exclusive control of processes, but whatever may be the policy as to the trade secrets, exclusive control by the industry, or secrecy in institutional research, it is my opinion that there is an urgent and immediate need of a promoting and coördinating agency to foster general petroleum research and which will accelerate the acquisition of information to be obtained from the various research organizations of work in progress and contemplated. Quantity of research may be increased and the quality thereof enhanced through proper coördination and supervision.

A hearty coöperation may be expected from the scientist if he can be assured that the results of his investigation are given publicity.

As director of research of the American Petroleum Institute, I have received many recommendations as to the character of research that should be undertaken and without authorship or justification and without attempt to classify these problems as to the order of importance or according to their merits, I submit them to the corporations, the individuals, the chemists, and the engineers for their consideration. It is to the open field of prospecting that I am trying to direct the scientific discoverer. It may be that some of these problems are old and some are new, but in whatever category they fall, a discussion which I hope will follow these recommendations will be disclosed by those who have been the pioneers of the past.

As one who can speak with authority on some of the lessons we learned from the war, I want to say to you directly that the greatest lesson of all to me was the mobilization of the scientific experts for chemical warfare investigations which was so quietly, quickly, and efficiently accomplished and which developed into a technical enterprise of tremendous importance and of which so little has been said. Such an accomplishment has its influence on a peace-time program which I now offer to you.

The following are suggestions from American research chemists and engineers.

The petroleum problems in this list are subdivided under the four operating branches of the industry:

1—Production.
2—Transportation and storage.
3—Refining.
4—Marketing and utilization.

Each problem is classified as an "A" or "B" problem. "A" problems are of known importance, the solution of which will be of material benefit to the industry and the nation; "B" problems are of indeterminate importance and arise through a lack of knowledge; study and solution of these problems may or may not develop results of practical value.

PRODUCTION PROBLEMS

1—An investigation of the use of charcoal, silica gel, and iron gel for the recovery of gasoline from casinghead and refining gases, including an examination of the character of the recovered product and the thermal efficiency of the process in comparison with oil recovery methods. (B)

2—A broad study based on thermodynamic principles of gasoline recovery processes including the application of refrigeration to casinghead and refining gases and development of more efficient methods and mechanical equipment in a manner similar to the work of Norton in recovering helium from natural gas. (A)

3—An investigation of blending volatile casinghead gasoline and naphtha with special reference to the economic limits of blending. (A)

4—Breaking up of water-oil emulsions with maximum oil recovery and the prevention of ingress of water into the oil well. (A)

5—Increasing recovery from wells; reviving old wells. (A)

6—A chemical study of underground water in relation to oil production. (B)

7—Shale oil development. (A)

TRANSPORTATION AND STORAGE PROBLEMS

1—A comprehensive study of fire fighting and prevention methods with respect to all phases of the petroleum industry. (A)

2—Study of methods for cleaning and freeing tanks and bunkers of inflammable vapors prior to making repairs; the development of simple methods for testing such tanks to determine if they have been freed from vapors. (A)

3—Study of the protection of men from noxious gases and other hazards in the entire petroleum industry; use of gas masks, breathing apparatus; designing tanks and apparatus so that men need not enter the noxious atmospheres. (A)

4—Investigation of storage and transportation losses and development of methods for minimizing this loss. (A)

5—Effective vapor pressures in tank cars, etc. (A)

6—Thermal expansion of petroleum as affecting measurements. (A)

7—Cement storage tanks. (B)

REFINING PROBLEMS

1—Recovery of gasoline from refinery gases. The importance of this problem has already been recognized and recovery plants (generally of the absorption type) are in use in various refineries for the removal of gasoline from still gases. An educational campaign should be instituted to advise refiners of the advantages of this procedure and, in addition, the recovery of gasoline from all refinery gases, pressure stills, agitator tanks, etc., should be considered. Relative efficiency of solvent absorbents, charcoal and silica gel and ferric hydroxide gel should be investigated. (A)

2—Recovery of other chemical products from refinery gases:

(a) Propylene and ethylene for making alcohols, glycols, etc. (B)
(b) Chlorinated products, artificial resins, isoprene. (B)

3—Recovery of chemical products from acid sludges. (B)

4—Conservation of chemicals used in the treatment of petroleum products:

(a) Decreased use of sulfuric acid. Many products are probably treated more heavily than is necessary to insure satisfactory utilization. (A)

(b) Closer utilization of alkali. Many refiners simply make sure they have an excess in their treaters and do not attempt to hold this excess down to a satisfactory minimum. (B)

(c) Wider use of sulfuric acid recovery plants. Application to needs of small refineries. Investigation of best type of equipment. (A)

(d) More economical use of filtering clay and fuller's earth. (A)

(e) Study of most favorable conditions, temperature, time, etc., for chemical treatment. (B)

5—Increased fuel economy (fire box to oil). There is a notorious waste of fuels in refineries. Extended investigations of proper fuels and of furnace design will result in saving much fuel. (A)

6—Improved design and insulation of stills and fractionation towers. Heat losses can thus be cut down and efficiency will be increased. (A)

7—Utilization of heat liberated in condensing the vaporized oil. Considerable heat is now lost which can be saved by suitable preheaters or heat exchangers. (A)

8—Increased use of continuous distillation equipment. Development work with different types of oils is required to extend use of continuous distillation. (B)

9—Increased use of continuous treating equipment which when fully developed for various oils will result in greater efficiency of operation. (B)

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10—Increased use of fractionating columns on stills will give larger yields of valuable gasoline fractions. There is need for thorough scientific investigation of fractionating columns. (A)

11—The prevention of entrainment by more efficient separating devices. The adoption of such equipment will permit much higher distillation rates than those now customarily employed. (A)

12—Development and improvement of cracking processes and increased use of same:

(a) For increased production of gasoline. (A)
(b) For distillation to coke of oils having high content of asphalt. (A)
(c) For production of lubricating oils as through use of $AlCl_3$ or similar agents. (B)

13—Improved methods of filtering lubricating oils. Use of other material than Florida clay or fuller's earth and the revivification and more economical use of filter materials. Possibilities of activated charcoal, silica gel, and iron gel should be investigated. (A)

14—The use of solvents for the removal of color from spent fuller's earth. (B)

15—The fractionation of petroleum residues containing paraffin wax into distillate and undecomposed amorphous wax; and the elimination of gummy or asphaltic portions from wax distillate by a distillation or mechanical procedure. (B)

16—Study of nature and distribution of sulfur derivatives in petroleum. Improved methods of removing sulfur from crude oils and distillates especially by the use of absorbing agents and a study of methods for controlling the distribution of sulfur among the various products. (B)

17—A thorough study of the mechanical and chemical efficiency of distillation methods as applied to various types of petroleum with special reference to the development of flexible refining methods which permit the maximum production of products for which there is the largest demand. Under this head is included a study of cracking, topping, and straight cut distillation. (A)

18—A thorough investigation of the progressive deterioration of stills with reference to the prevention of explosions and the reduction of life and fire hazards. (A)

19—Standardization of analytical methods, including improvement of many present methods and development of new methods. (A)

20—Study of physical and chemical constitution of different types of crude petroleum to provide necessary fundamental data now lacking. (B)

21—Study of various chemical reactions of petroleum hydrocarbons, particularly oxidation, hydrogenation, and halogenation. Such study may lead to the manufacture of valuable base materials and intermediates for the production of organic chemicals and dyestuffs. (B)

22—Study of nature and behavior of crystalline and amorphous paraffin wax in petroleum; and investigation of wax chillers. (B)

23—Investigation of production of special products, such as:

(*a*) Harder grades of wax. (B)
(*b*) Wool oils. (B)
(*c*) Polymerized olefins. (B)
(*d*) Benzene and toluene. (B)
(*e*) Organic acids and alcohols. (B)
(*f*) Drying or siccative oils. (B)
(*g*) Isoprene. (B)
(*h*) Dyestuffs. (B)

24—A study of the properties required of oils for use in absorbing benzene, toluene, etc., from artificial gas or in solvent recovery system. (A)

25—Thorough study of the relation between chemical constitution of oil and its lubrication properties with a view to so treating oils as to increase their lubricating power. (B)

26—A physicochemical study of the structure and properties of greases. (B)

27—Study of methods for reducing the viscosity of Mexican fuel oil so as to eliminate the necessity of preheating. (A)

28—Dehydration of crude oils and oil emulsions, including study of comparative efficiency and costs of the following methods:

(*a*) Electrostatic. (A)
(*b*) Centrifuging. (A)
(*c*) Heating. (A)
(*d*) Miscellaneous methods. (A)

29—A study of the influence of various types of electrical discharges and other electrical effects on cracking of oils. (B)

MARKETING AND UTILIZATION PROBLEMS

1—Preparation of rational specifications for petroleum products; these specifications to be based upon the results of actual research work. More rational volatility specifications for gasoline and tests for the "oiliness" property of lubricants are especially desirable. (A)

2—Standardization of analytical methods and apparatus for testing and analysis of petroleum products. (A)

3—Utilization of wider range of motor fuels in mobile types of engines (autos, trucks, tractors, etc.). (A)

4—More efficient utilization of heavy oils in Diesel and other engines of the heavy oil type. (A)

5—Investigation as to the actual need of highly refining gasoline for motor fuel; is it necessary to remove bad smelling sulfur compounds completely in order to obtain efficient service from gasoline? Will these compounds injure the engine? If high degree of refinement proves unnecessary educate the public to use less highly refined products and thus increase the yield and lower the cost. (A)

6—Development of higher efficiency in internal combustion motors through use of selected fuels (naphthene or aromatic mixtures) or through use of chemically treated fuels which will stand higher compressions. Applies especially to aeroplane engines. (B)

7—Modify the design of carburetors and internal combustion engines so as to enable the use of less volatile gasoline, and investigate the relations between volatility, specific gravity, and distillation analysis to performance in automobile engines; relative performance of blended mixtures and straight cuts. (A)

8—A study of the fundamental causes of carbon formation in cylinders; elimination of polymerized products in cylinders; study effect of additions of peroxides, naphthalene, picric acid, phenanthrene, pyrene, picene, cyclohexanol, phenol, etc. (A)

9—Combustion characteristics of different hydrocarbon series. (B)

10—Ignition temperature, detonation, etc. (B)

11—Effect of volatility on fuel consumption. (B)

12—An unbiased scientific study of the differences in properties and behavior of oils from different base crudes and the fundamental causes thereof. (B)

13—A study of the relative tendency of different lubricants to absorb fuel and become excessively diluted. (A)

14—Scientific study of numerous problems in lubrication. (A)

15—Recovery and purification of used lubricating oils in large industrial plants. This would be in the interest of conservation. (B)

16—The prevention of oxidation of mineral oils in transformers. (B)

17—Development of satisfactory small-scale oil-gas apparatus for use in country homes and small villages. (A)

18—Development of household oil heating devices. Why not use oil in the furnace? It should be as convenient as gas with proper equipment. (A)

19—More effective utilization of the butanes and pentanes in natural gas gasoline and in light petroleum fractions. Much of this is now lost by evaporation. (B)

20—Utilization of larger proportion of petroleum coke produced. Owing to impurities much of this coke is not suitable for carbon products. Elimination of impurities and improvement of quality should be investigated. (A)

21—Production of oil-gas and also hydrogen by cracking natural gas, or petroleum vapors with the production of a carbon black that will meet the same requirements as carbon black made by the incomplete combustion of natural gas. (B)

22—A broad physicochemical study of the production of carbon black, with a view to the discovery of more efficient methods than wasteful partial combustion process. (B)

COLLOID CHEMISTRY

In view of the importance of colloid chemistry in connection with the petroleum industry, I wish to stress particularly the need for the study of various problems in this industry from the colloid chemistry standpoint.

As topics for major problems, the following have been suggested, some of which have been mentioned heretofore in this paper; however, it is believed worth while to group them under this heading:

1—A thorough study of the properties and behavior of emulsions including:
(*a*) Mechanism of the formation and stability of various emulsions. (*b*) A study of the nature of emulsifying agents. (*c*) Methods of breaking. (*d*) Comparison of properties of emulsions obtained from different base oils. (*e*) Study of various emulsion products, such as cutting oils and greases.

2—A thorough study of lubrication from a colloid chemical standpoint.

3—Investigation of the properties and behavior of crystalline and amorphous wax.

4—A study of the application of the adsorptive action of various substances, such as bauxite, fuller's earth, silica gel, iron gel, etc., with reference to the following problems:

(*a*) Recovery of gasoline from refinery gases.
(*b*) Desulfurization of both light and heavy fractions.
(*c*) Removal of coloring matter.

5—A thorough study of the properties and utilization of various grades of asphalt.

AMERICAN CHEMICAL SOCIETY SUGGESTIONS

At the meeting of the Petroleum Section of the American Chemical Society which was held in New York City in 1921, the following subjects were recommended as suitable fields for research:

1—The chemistry of petroleum hydrocarbons, particularly of the higher homologs.

2—The chemistry of the sulfur, nitrogen, and oxygen compounds in petroleum.

3—The chemistry of sulfuric acid refining of oils.

4—The chemical and physical changes undergone by lubricating oils used in continuous systems.

5—The causes and mechanism of color changes in oils.

The list might be supplemented almost indefinitely from the fields of fuel and lubrication.

Suggestions from an English Chemist

In considering the directions in which organized scientific research for the benefit of the petroleum industry can now be set on foot, it appears to me that before proceeding to enumerate a series of definite problems for investigation there are some general considerations which ought to be put on record.

Group at Sheffield, Ala., before Visiting Nitrate Plants

At about the middle of the last century the development of the steam engine had reached such a stage that before any further vital improvements could be made and measurements of engine efficiency carried out it became essential that the fundamental physical data relating to the properties of water and steam should be determined with a great deal more accuracy than that attained at the time. The classical work on the steam engine done by Regnault and his colleagues under the auspices of Emperor Napoleon III over a period of about thirty years has been until quite lately the basis on which all computations relating to steam engineering were founded. In my view the time has now arrived when, in the interests of the use of oil fuel of all kinds, particularly in the various forms of internal combustion engine and in large steam boilers, a similar comprehensive series of determinations of fundamental physical and chemical constants should be carried out by a competent organization. With the support of the combined oil interests, an attempt should be made to improve the technic of the various processes of the mineral oil industry, and to this end a comprehensive and systematic series of chemical and physical investigations is required.

1—It is of course known that nearly all petroleum products, whether light, medium or heavy oils or solids, are not simple chemical substances, but complex mixtures, whose single constituents are often difficult to separate from one another. But this difficulty of preparation furnishes no excuse for our present lamentable ignorance of the fundamental properties of many of these important bodies, now consumed to the extent of many millions of gallons annually. I am not exaggerating when I say that the only data we possess as to many of these substances depend on determinations carried out years ago on quite small quantities by investigators whose competence and equipment left much to be desired, and that in many cases the purity of the substances in question was, to say the least of it, extremely doubtful. I think, therefore, the time has now arrived when an attempt should be made to prepare in quantity in a state of high purity all the more important members of at least three of the main chemical series, the normal hydrocarbons having the formulas C_nH_{2n+2} C_nH_{2n} and C_nH_{2n-2}. When these have been properly studied it will then be possible to proceed to a certain number of the iso and cyclo bodies of corresponding formulas. The study should include not only the usual properties mentioned in the textbooks, but determinations of the flash point and firing point of each, as well as fairly complete measurements of the vapor pressure of the more important members from quite low temperatures below the freezing point of the substances up to and beyond their boiling point—in fact, a systematic extension of the classical work of Ramsay and Young.

2—Bearing in mind that practically all commercial oils are mixtures of several homologs, it will be desirable that as soon as the requisite knowledge of the fundamental properties of the pure constituents has been obtained, a study should then be organized on certain mixtures, and that the laws regulating the dependence of the physical properties of a mixture of oils on those of its constituents should be investigated. Thus it is highly desirable that we should know more of the nature of the vapor pressure curves of mixtures, and should be in a position to predict more accurately, for example, the influence on the vapor pressure and flash point of a given addition of low-flash oil to one of lower volatility.

3—Up to the present time the thermal properties of most organic substances have been investigated by means of the calorimetric bomb. In the opinion of many of those who have used this instrument it possesses very grave disadvantages, particularly for application to extremely volatile oils. Indeed, under many circumstances the determination of the heat of combustion of such a substance as petrol by means of this instrument may be dangerous, even though quite small quantities of substance are used. In my view it is urgently necessary that as a preliminary to the program of systematic work outlined above, a design should be worked out for a new calorimeter, which would probably be of the flow pattern in which accurate results could be obtained for the gross and net calorific values of low-boiling organic substances.

4—An urgent requirement of the petroleum industry is that more precise and detailed instructions should be prepared and apparatus devised for carrying out the different standard tests prescribed. In 1912, at the Vienna Congress of the International Petroleum Commission, proposals were made as to the standardization of the different types of flash point tester, and it was shown that the original apparatus as devised by Sir Frederick Abel, the modified form used in the British Colonies, and the later German form differed systematically in their indications by amounts which were too serious to be ignored. The work of the British National Physical Laboratory and of the American Bureau of Mines in investigating the causes of these systematic differences should be continued, with a view, at a later stage, to some ultimate international agreement being arrived at on all the more important tests on the different kinds of oil products.

One of the most urgent directions in which further work of this kind is required is in connection with very low flash points, since the methods and apparatus of Abel are quite unsuited for work at low temperatures. Tests comparable with the Abel test, and a proper form of apparatus for the same, need to be worked out for motor spirit of all grades. In the apparatus for this test a suitable cooling arrangement would take the place of the water bath and burner.

Similarly, the investigation of viscosity by the various types of apparatus in use greatly requires systematizing, and the true relation between viscosity, lubricating value, and chemical composition requires more detailed investigation. In view of the widespread introduction of heavy fuel oil into marine work, the whole question of the viscosity and setting points of heavy oils needs much further systematic study, in order that the problems arising in connection with the storage and transport of heavy oil may be adequately dealt with.

5—It is very desirable that the limits of explosibility of oil vapors with air and oxygen should be more thoroughly investigated than at present, and the influence of pressure and temperature on these limits should be studied over a considerable range.

6—It is well known that in the cracking process the general basis of the reactions occurring is that heavy hydrocarbons can be made to split up into bodies consisting of smaller and lighter molecules. In general it is found that a body of the formula C_nH_{2n+2} splits up into two smaller portions of half the molecular weight. It would, however, in general be more advantageous if the cracking could be so designed that instead of division of a long chain-type molecule into two equal portions, the severance could be made in such a way that the pieces were more like two-thirds and one-third or three-fourths and one-fourth, seeing that nowadays the object of nearly all cracking is to obtain a large proportion of the lightest possible spirit. An extension of such work as that of Rittman in America and of Ashcroft in England, with a view to determining the conditions favorable to the formation of low-boiling hydrocarbons of the paraffin series, as well as of the lower members of the aromatic series, is one of the most urgent lines of new investigation. It should be undertaken, in the first instance, not by engineers but by physical chemists having a thorough knowledge of phase-rule chemistry and reversible reactions. Engineers can afterwards be called upon to build up manufacturing processes upon the foundation thus laid.

The use of catalysts in facilitating the production of lighter hydrocarbons from petroleum should also be systematically studied. Already promising results have been obtained on the application of catalysis to the production of petrol.

7—In the utilization of motor spirit many inconveniences are caused if the spirit in question contains hydrocarbons which tend to become gummy. It is well known that cracked spirit, the use of which is rapidly extending, contains bodies in which spontaneous slow changes may subsequently take place, and a grade of spirit having no objectionable properties when fresh may polymerize or suffer slow oxidation, and the percentage of hydrocarbons of a gummy character may become greatly increased merely on standing. The cause of this phenomenon is very obscure, and it is desirable that the nature of those bodies which are objectionable should be thoroughly investigated and that the changes which go on in cracked spirit, tending to restrict its usefulness, should be properly studied, with a view to mitigate or prevent them completely.

SUGGESTIONS FROM AMERICAN MECHANICAL ENGINEERS. PROGRAM OF INVESTIGATION OF FUELS USED IN INTERNAL COMBUSTION ENGINES

For the purpose of increasing combustion efficiency, reducing noxious quality of exhaust gas, development of wider range of fuel, and reduction of waste through imperfect combustion.

1—Influence of composition of fuels on composition of exhaust gases.

Effect of physical properties of fuel:

(*a*) Volatility.
(*b*) Distillation range.
(*c*) Viscosity.
(*d*) Density.

Effect of chemical properties:

(*e*) Chemical composition.
(*f*) Ratio of carbon to hydrogen.
(*g*) Degree of unsaturation.
(*h*) Addition of substances to improve combustion or prevent detonation.
(*i*) Effect of catalyzers.

2—The behavior in internal combustion engines of liquid fuels produced by different processes.

3—Experimentation with new type engines for tractors and trucks using low-grade fuels, such as topped oils, tars, etc.

4—Adaptation of engine structure to available fuels:

(*a*) Carburetor.
(*b*) Manifold.
(*c*) Compression.
(*d*) Ignition.
(*e*) Lubrication.
(*f*) Stroke, etc.

5—Standardization of oil well supplies.

6—Heat treatment of drill steels and development of improved drilling methods.

An American chemist comments as follows on a few problems selected at random from the preceding list.

DISTILLATION

In the distillation of kerosene, wax distillate and lubricating oils, steam is usually used with direct fire under the still, to prevent decomposition of the hydrocarbon oils treated. A thorough testing of vacuum distillation instead of the use of steam in the refining of kerosene, wax distillate, and lubricating oils should be worked out at a really low vacuum with the view of using low vacuum in the distillation of petroleum oils. The distillation of kerosene, gas oil, and residuum from paraffin, semi-paraffin and asphaltic oils under heat and pressure lend themselves to research so that industrial methods may be worked out to crack oils for general use by refineries.

SPECIFIC HEAT AND HEAT VAPORIZATION OF PETROLEUMS

The specific heat of liquids, latent heat of vaporization, and specific heat of the gaseous hydrocarbons and petroleum oils and their distillation products is of importance to the refiner. With a knowledge of these three physical constants one could calculate the square feet of heating area to a still, furnish construction, condensing areas of vapor lines and water condensing areas in closer agreement with what is required in commercial installations. They would be of high importance in the cracking of petroleum oils, in working up ratios of heating surface of the still to the vapor line, aerial condensers and water condensers per gallon of oil treated, per gallon of pressure distillate, and per gallon of gasoline made per unit of time.

TREATMENT OF DISTILLATION PRODUCTS OF PETROLEUM

Investigation of the use of other acids than sulfuric in the refining of petroleum distillates with a view to finding reaction products which will lend themselves to further chemical products for commercial use. There seems to be no doubt that for certain oils hydrochloric acid would give hydrocarbon chlorides which upon hydrolysis would yield alcohols for use perhaps in the formation of condensation products useful as insulation material and for other purposes.

FILTERING MATERIALS IN REFINING

Fuller's earth and a number of re-burnings of the same for re-use with control factors such as microscopic examination during burning. Investigation as to the factors involved such as absorption phenomena as a function of the size of the particles. Also the regeneration of the filtering qualities of the earth while still on the filter bed, instead of sending to "bone burning house" to be regenerated at high temperatures with incident depreciation of its filtering qualities.

SOLVENTS

Sulfur dioxide lends itself to the separation of hydrocarbon groups and should be studied on a semicommercial scale, with a view to separating the particularly interesting groups of naphthene hydrocarbons which are so abundant in some of our crude oils. This might well lead to a whole series of commercial dyes being made, from the naphthenes as a base. Alcohol and other solvents should also be studied.

CONSTITUENTS OF PETROLEUM

The work of Warren and Mabery on the constituents of petroleum oils has been of the highest value to every one connected with the scientific as well as the technical side of the petroleum art. However, our knowledge is meager compared to what is yet undone. For illustration, our knowledge of the constituent hydrocarbons making up lubricating oils is well nigh a blank, and so much depends upon the quality of these oils. A thorough knowledge of the properties of these hydrocarbons would throw a flood of light upon just what hydrocarbons have the lubricating qualities for the specific work in hand—such as for aeroplane use in warfare, where so much depends upon superior oils. To get at the whole lubricating problem, it seems to be necessary to know the hydrocarbons in the lubricating oil before one can state what it is that gives an oil the quality of adhering to two surfaces without breaking down under the temperatures and pressures of the surfaces.

Old Tannehill Furnace, Republic Iron & Steel Company

Emulsion Oils

The production of emulsion oils in the United States is relatively large and much research is necessary so as to break down the emulsion economically. An immense amount of work is ahead to determine the characteristics of the varied emulsion crude oils and bottom settlings in tanks, for millions of gallons are wasted yearly as a result of the difficulty in handling this material. It is not clear as to how the water is dispersed in the hydrocarbon oils, but it seems reasonable to suppose that part of the water is present in the hydrated form, adding to the difficulties of handling the oil due to puking or frothing of the still charge when the hydrate breaks down into water and hydrocarbon liquid at a temperature above the boiling point of water. A suggested research would be to isolate a series of hydrocarbon hydrates from emulsion oils or to make a set from known hydrocarbons of varied molecular weight.

Elimination of Redistilling of Distillates from Crude Oils

A large saving in economic wealth could be obtained in the average refinery by installing proper fractionating columns upon the crude still so as to make one cut for finished gasoline without going through the usual redistillation of the crude gasoline ordinarily distilled off the crude. This holds for the kerosene cut also. This method of operation would cut down not alone the fuel cost but also the number of stills for a given output. The uncondensable gas loss in refinery practice is large but would be cut down by making one cut off the crude for its gasoline and kerosene content. The treatment with acid and caustic soda for the gasoline would be eliminated when using Pennsylvania and most of the mid-continent, Kentucky, and Virginia crude.

Gas Oil

More efficient methods of cracking gas oil into marketable gasoline and kerosene so as to cut down the excessive fuel cost involved in producing gasoline by the successful process now in use. Also to work out atmospheric pressure processes by the use of catalyzers. Increase fixed gas yields for heating and lighting purposes, to the gallon of gas oil from gas making apparatus. To utilize gas oil for more economic purposes than fuel oil.

Wax Distillate

The treatment of wax distillate in one stage to convert the amorphous wax into crystalline (so that it will readily press out in the filter presses) in the crude stills instead of the usual practice to recrack the wax distillate in another still cracking the same at atmospheric pressure. Centrifuging experiments for the removal of amorphous and crystalline wax from their hydrocarbon solvent.

Foots Oil

Foots oil is an intermediate cut from the wax distillate which is re-cycled and re-cycled in the refinery and contains wax which should be recovered. It would mean tons of wax a day recovery to the industry.

Lubricating Oil

The acid treatment of lubricating oils and the treatment of emulsions which occur from neutralizing and water treatment of the same after acid treatment. The distillation of the lubricating oils by means of vacuum instead of use of steam at atmospheric pressure should be tested out for economy and production. The problems in connection with filtering of lubricating oils to color, flash, fire, and viscosity and by the use of filtering materials that have specific action upon the different types of hydrocarbon, instead of as at present the use of fuller's earth and boneblack, would be valuable. Also the investigations of solvents for the refining of lubricating oils instead of acid and caustic treatment in filtering such as liquid sulfur dioxide and other solvents.

Casinghead Gas

To work up a series of commercial solvents which will have selective solubility for specific hydrocarbons in the casinghead gas so as to utilize the same for other purposes than internal combustion engine use.

Color of Hydrocarbon Oils

To determine the color from light lemon to deep red of the various petroleum products and what the colors are due to with a view to making water-white lubricating oils. My present view is that the color in the main is due to colloidal carbon. However, this has not been determined experimentally.

Tests of Petroleum Products

The present control of petroleum products is highly variable on account of the human element, making it difficult to check results in different parts of the country apparently using the same instruments. It seems necessary to work out tests that are practically mechanical in their operation, readily duplicable by any two operators and cutting out highly skilled technicians.

Sulfur Oils

Many suggestions have been made that investigations are necessary of the sulfur oils and gaseous products coming off the stills. These gases have a deleterious effect upon the health of the men; in addition a form of rash appears upon the skin, and they also cause conjunctivitis. It has been found that vapor and gases from the crudes containing a high sulfur content have a narcotic effect upon the workmen. The constituents of these gases are not known. It is known, however, that hydrogen sulfide is present but arsine and stibine have not been isolated, and it is of interest that the American Petroleum Institute and the United States Bureau of Mines have just started an investigation to cover the three fundamental factors involved: (1) to determine the constituents of these vapors and gases, (2) the amount of concentration, and (3) a gas mask to be developed to protect the workmen.

Some Physical Properties of Rubber Compounded with Light Magnesium Carbonate[1,2]

By H. W. Greider[3]

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Light magnesium carbonate is a light inorganic filler for rubber which has heretofore received little attention from American rubber technologists. In this paper there are given data showing that this material behaves as a typical reinforcing pigment, increasing the tensile strength, hardness, stiffness, and resilient energy capacity of rubber in which it is compounded. Comparison has been made between the physical properties of rubber compounded with magnesium carbonate and with other commercial rubber reinforcing fillers, including zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. The results indicate that magnesium carbonate is exceeded in reinforcing power only by gas black.

Special consideration is given to the principal disadvantage of magnesium carbonate in rubber, viz., the property of high permanent set imparted to the vulcanized product, which is attributable to the definite crystalline or nonamorphous character of the particles. The author believes that the application of the principles of colloid chemistry to the conditions of the commercial precipitation process will enable this material to be prepared in an amorphous form which will make it much more valuable as a rubber compounding material, by reducing the objectionable permanent set and enhancing the tensile strength and toughness of rubber compounded with it.

LIGHT magnesium carbonate, the chemically precipitated basic hydrated carbonate of magnesium, is not a new compounding material to the rubber industry of this country although it has never had the extensive and general use as a toughening and reinforcing filler in American rubber compounding practice which it has found in British and Continental rubber manufacturing. The English rubber chemist's knowledge of and experience with magnesium carbonate is, therefore, considerably greater than our own. The reason for this may be explained by the fact that rubber compounding practice has developed along rather different lines in this country from in Europe, particularly with respect to the adoption of gas black as a reinforcing pigment. The future for gas black does not seem particularly encouraging at this time owing to the rapidly decreasing supply of natural gas available for its manufacture and to various actual or threatened legislative restrictions on the use of natural gas for the production of this material. The rubber industry is, therefore, very properly concerned with the discovery of new, light, inorganic, "active" fillers, and is interested in the further development and improvement of those which it already uses. Some American rubber manufacturers use considerable amounts of magnesium carbonate; others use very little or none at all, and it is believed, therefore, that some of the data here presented, on the physical properties and mechanical behavior of rubber compounded with light magnesium carbonate, will be of interest to those rubber technologists who have not previously given this material much attention or study.

The raw material for the manufacture of light carbonate of magnesia is dolomite rock, high magnesian-limestone, of which there are enormous deposits in this country and, in fact, all over the world, so that there is no possibility of a future exhaustion of the raw material supplies for the manufacture of this product. A number of the deposits which are being worked commercially at the present time are in Pennsylvania, convenient to the manufacturing centers and markets of the Eastern and Central States. The companies now manufacturing light magnesium carbonate have producing capacity ample to supply any possible needs of the rubber industry without the installation of additional equipment. It should be remarked that, since magnesium carbonate is manufactured by a chemical precipitation process, its production cost will necessarily be greater than the costs of naturally occurring materials which require only a minimum amount of treatment to prepare them for use in compounding; the principal factors in the cost of magnesium carbonate being coal and labor, both of which items may be subject to some downward revision in the future.

Basic magnesium carbonate may be manufactured from any soluble magnesium salt by treating it in solution with an alkali carbonate, but the product so obtained is likely to be rather variable in composition and not extremely finely divided. The light carbonate offered to the rubber industry as a compounding material is prepared commercially in this country by the rapid heating of a solution of magnesium acid carbonate, and this process gives a very white, soft, bulky, finely divided form of the material, of uniform composition. The formula ordinarily given for the composition of the substance in the dry form is $4MgCO_3.Mg(OH)_2.5H_2O$, but numerous analyses of the commercial material seem to indicate that it corresponds actually more nearly to such a formula as: $11MgCO_3.3Mg(OH)_2.11H_2O$. The composition varies slightly according to the conditions obtaining in the production processes, particularly the concentration of the magnesium acid carbonate solution and the rate of heating of this solution, but under rigid control of the process the composition of the product will be constant. The commercial carbonate of magnesia is usually practically chemically pure, containing only traces of iron and alumina, no silica, and considerably less than 1.0 per cent of lime as calcium carbonate. On samples free from hygroscopic moisture it gives an ignition loss varying from about 54.5 to 56.8 per cent. At ordinary temperatures it is inert to most chemical influences except the action of acids, which dissolve it, forming soluble magnesium salts. No decomposition takes place on heating to temperatures below 265° C. (509° F.), a temperature much above that to which rubber products may be safely subjected, either in the vulcanization process or subsequently. It seems probable that the water in the above chemical formula for the material is not ordinary water of crystallization, but water of constitution.

With regard to its use in rubber, its volume cost per unit of reinforcing effect, or per cubic foot of rubber compounded with it, will be small, owing to its low density, and considerably less than that of heavy pigments, such as zinc oxide or barium sulfate.

Light magnesium carbonate has an absolute density of about 2.18, although some figures rather lower than this have been given. It is, therefore, one of the lightest of the min-

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[1] Received March 25, 1922. Presented before the Division of Rubber Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922

[2] The data presented in this paper summarize the more significant portions of the results of an investigation of this material, carried out at the Mellon Institute of Industrial Research, for the Magnesia Association of America.

[3] Industrial Fellow, Mellon Institute of Industrial Research.

eral inorganic fillers and gives a vulcanized rubber of low specific gravity, although somewhat higher than that given by gas black or lampblack. The individual crystals have a distinct acicular crystal form and are very friable. Examination under the microscope shows an average particle size of somewhat less than a micron, with a few larger crystals, although the particle size varies somewhat in the product of different manufacturers and will depend on the control of the conditions of precipitation and upon the completeness of the pulverization process. The carbonate shows only a very slight solubility in water, about 0.035 g. of the oxide dissolving in a liter, and giving the solution a reaction alkaline to thymolphthalein indicator.

Except with respect to investigations of the effects of various mineral and organic accelerators, there has been, until recently, but scant information regarding compounding ingredients in the literature of rubber technology. Toughening and reinforcing fillers were, of course, always differentiated in the practical work of the rubber technologist from ordinary coarse fillers and inert pigments, but very little data comparing the actual physical behavior of different fillers in rubber were published until W. B. Wiegand[4] studied the effects on the stress-strain relationships of rubber, obtained with several common compounding materials, and brought forward the concept of energy of resilience in rubber. Wiegand divides all rubber fillers into two groups, according to whether the average particle size is extremely small or whether the particles are relatively coarse. The reinforcing effect of rubber pigments he considers to be a function of the surface area exposed to the rubber by unit volume of the material, aside from specific surface and cohesion effects and, therefore, dependent upon the fineness of division of the particles. He succeeded in showing that all the rubber fillers he studied, which modify the stress-strain curve in such a way as to enable the rubber to exhibit high total resilient energy, are those which are very finely divided. These fillers, which are relatively few in number, he designates as "active" fillers or reinforcing pigments, whereas the coarse fillers, which do not greatly modify the stress-strain curve and, therefore, only dilute the rubber and attenuate its tensile strength, ultimate elongation, and resilient energy capacity, in whatever proportion they may be used, he refers to as physically inert fillers. Resilient energy capacity, according to Wiegand, is a measure of the reinforcing or toughening effect obtained with various fillers and he relates it also in a theoretical way to abrasive wear resistance.

Wiegand did not include light magnesium carbonate among the rubber pigments studied by him, and aside from mere occasional mention of its action as a mild accelerator of vulcanization, the work of C. O. North[5] seems to be the only investigation so far published in which the behavior of this material in rubber is described. North made a comparative study of zinc oxide, gas black, magnesium carbonate, lithopone, barytes, and tripoli flour, in mixes containing rubber and sulfur only, with respect to the effects of these fillers on the physical properties of the vulcanized rubber. He found that, in the type of basic mix he used, magnesium carbonate gave its maximum effect on tensile strength at six volumes of the carbonate to each one hundred volumes of rubber, this tensile being higher than that obtained with any other filler, except gas black. For proportions of magnesium carbonate between six and fifteen volumes per one hundred of rubber, he obtained values for tensile strength "corrected" to the basis of 100 per cent rubber in the stock, which were equal to or slightly greater than the highest values obtained for zinc oxide, but not as great as given by larger proportions of gas black. For the same proportions of magnesium carbonate he obtained calculated values for tensile product and for tensile product "corrected" to 100 per cent rubber, which were greater than similar values obtained for gas black, zinc oxide, or the other fillers studied. This last result means, of course, that magnesium carbonate gives rubber having high tensile strength combined with high ultimate elongation values. North also gave data showing the high permanent set given by magnesium carbonate and attributed to this effect the fact that American compounders had not used this filler to a very great extent.

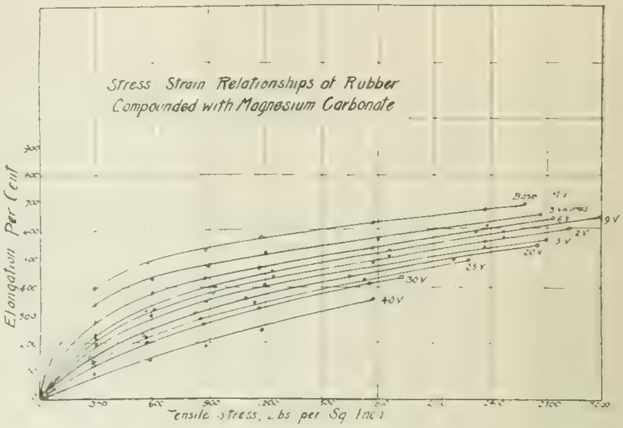

FIG. 1

EXPERIMENTAL METHOD

All the rubber samples described in this paper were prepared under experimental conditions maintained as nearly uniform as possible, with respect to the composition of the basic mix, incorporation of the fillers on the mill, calendering, and vulcanization. The basic mix adopted had the following composition in parts by weight:

First quality pale crepe	100
Litharge	30
Sulfur	5

This basic mix is similar to that used by Wiegand in the investigation referred to above, except that pale crepe rubber was used in place of fine Para. The difficulty in obtaining a satisfactory grade of cleaned and dried Para at the time this work was begun made this change seem advisable. In parts by volume this mix contains:

First quality pale crepe	100
Litharge	3
Sulfur	2.5

The purpose of using this type of basic mix containing a considerable excess of litharge as accelerator was to make it possible to cure all the samples for a fixed period of time and to avoid the preparation of a series of cures for each proportion of filler of which the effect was to be studied. The values obtained for physical properties should also be somewhat nearer to those which can be produced in the factory than is likely to be the case in samples cured for a longer period with sulfur only, where the harmful effects of the longer period of heating on the samples may vitiate the results.

In this work two different lots of pale crepe rubber were used. The first lot, used in preparing samples compounded with various proportions of magnesium carbonate, gave a practically flat state of cure curve (judged from tensile strength values) over a curing period from 40 to 50 min. at 42 lbs. steam pressure (143° C.) when the samples were vulcanized in one-eighth inch thick sheet-molds in a press at 2500 to 3000 lbs. pressure. The basic mix sample showed its optimum aging qualities, both with respect to accelerated aging and weathering tests, when cured 45 min., and the same was found to be the case when the stock contained 15 volumes magnesium carbonate, and this was, therefore, selected as the curing period for all samples prepared from this lot of rubber. The second lot of rubber used in preparing stocks in which magnesium carbonate and other fillers were compared, was found to give its optimum cure, both with respect to tensile and aging qualities at a 49-min. period, which was, therefore, adopted as the best cure for all samples prepared from that lot. It was found, in curing samples prepared from both these lots with sulfur only, that both were decidedly slow curing in the absence of an accelerator. No difficulty was experienced in obtaining satisfactory cures in the litharge-pale crepe mix described above and the results obtained may easily be duplicated. The excess of litharge used was sufficiently great so that no difference in the cures when larger proportions of magnesium carbonate were used was observed, although North's[5] data showed that in a rubber-sulfur mix the accelerating effect of the larger proportions of magnesium carbonate was quite appreciable. Rubber cured with an excess of litharge accelerator was found to be considerably stiffer and much less extensible than when cured with sulfur only.

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[4] *Can. Chem. J.*, **4** (1920), 160; THIS JOURNAL, **13** (1921), 118.

[5] *India Rubber World*, **63** (1920), 98.

Three series of rubber samples were prepared to obtain the data given in this paper. In the first series the samples were compounded with proportions of magnesium carbonate varying from three to forty volumes per one hundred volumes of rubber in the compound. In the second series light magnesium carbonate in the proportion by volume found to give the maximum reinforcing effect (nine volumes) was compared with four other inorganic reinforcing fillers in the same volume ratio: zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. Rubber stocks compounded with mixtures of light magnesium carbonate with these same fillers, varying the proportions by regularly spaced increments, but maintaining the same total number of volumes of filler in each compound, were also studied. The third series included samples compounded with twenty volumes magnesium carbonate, with twenty volumes zinc oxide, and with various mixtures of these two fillers, having in each case a total of twenty volumes filler in the compound.

The materials used in the preparation of these rubber stocks were the best standard materials available in the market for use in rubber compounding, including zinc oxide of the highest quality, a superior grade of gas black, and impalpable sulfur. The china clay was a finely divided material especially prepared for rubber compounding and the colloidal barium sulfate was a high quality, highly dispersed product much superior to ordinary barytes. The magnesium carbonate was the ordinary light technical grade.

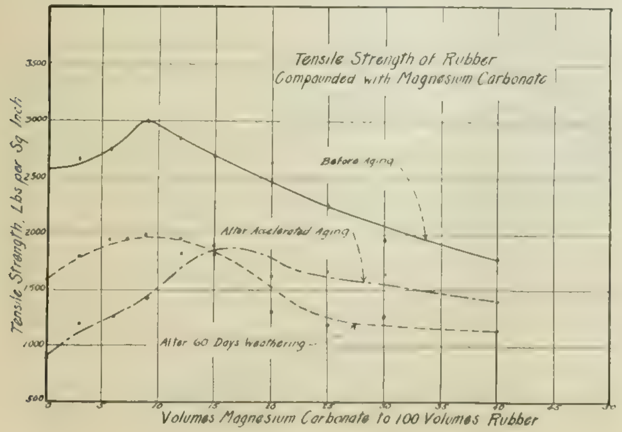

FIG. 2

PHYSICAL TESTS

The physical tests carried out upon all the samples discussed in this paper included:

TENSILE STRENGTH AND ULTIMATE ELONGATION—These values were obtained on a Scott testing machine using standard 0.25-in. width dumb-bell test strips. The results accepted as representing the actual values for these properties are in every case the average of the results from not less than five samples from the same sheet, the principle having been adopted of discarding results which were at great variance with the average and those in which premature failure of the test piece was obviously due to flaws in the sheet. Complete stress-strain curves for all the samples were obtained on the Scott testing machine, using two observers to secure the readings for the points on the curve.

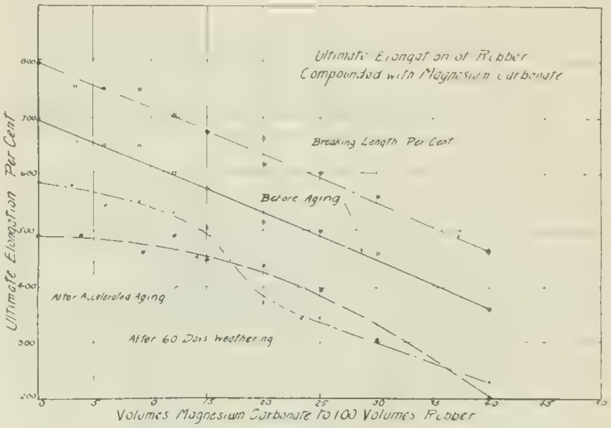

FIG. 3

TENSILE STRESS AT 300 PER CENT ELONGATION—The value for the load at 300 per cent elongation for each sample was obtained directly from the stress-strain curve plotted from the data obtained as just described.

TOTAL ENERGY OF RESILIENCE, AND ENERGY ABSORBED AT 300 PER CENT ELONGATION—Total energy of resilience was obtained according to the method of Wiegand, calculating from the area between the complete stress-strain curve and the elongation axis, and using a planimeter to determine this area. The energy absorbed by the rubber up to an elongation of 300 per cent was determined in the same way, using the planimeter to determine the area between the portion of the stress-strain curve below 300 per cent elongation, and the elongation axis.

PERMANENT SET—This property was determined by the method recommended by the Physical Testing Committee of the Rubber Division, using three stretches of the test piece to 60 per cent of the breaking length, with 5-min. rest intervals, and a final 10-min. rest before reading the permanent length deformation. The values given are the average of several tests on strips from the same sheet.

HARDNESS—The hardness of the samples was determined by means of a "durometer," a simple instrument depending on the penetration of a blunt point into the surface of the rubber sheet when a fixed pressure is applied. The range of hardness of vulcanized rubber is divided into an arbitrary scale, from "soft" at zero to "hard" at 100. The litharge-pale crepe basic mix used in this work gave a "durometer" hardness number varying from 40 to 42, depending upon the lot of rubber used. The hardness increases slowly with aging of the samples.

TENSILE PRODUCT—Calculated as tensile strength in lbs. per sq. in. multiplied by ultimate per cent length, and for convenience of numerical expression divided by 10,000.

ACCELERATED AGING TEST—All samples heated for 7 days at 71° C., in an oven through which a slow current of air was passing. This is considered to have approximately the same effect with respect to loss of tensile strength as 3.5 yrs.' aging under normal conditions.

WEATHERING TESTS—The samples subjected to this test were exposed to the atmosphere upon the roof of the building for 60 days during the summer months; this was a very severe test with respect to surface cracking tendencies and loss of tensile strength, and very few samples in the basic mix referred to above stood up well under this test.

TABLE I—DATA ON LIGHT MAGNESIUM CARBONATE

Volumes Light Magnesium Carbonate to 100 Vol. Rubber	Compound Composition by Weight—Per cent				Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Tensile after 60-Day Weathering Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Ult. Elong. after 60-Day Weathering Per cent	Permanent Set Per cent	Durometer Hardness Number
	Rubber	Sulfur	Litharge	Light Magnesium Carbonate								
0[1]	74.0	3.70	22.3	0	2575	872	1600	696	490	585	5.5	40
3	70.4	3.52	21.2	4.9	2670	1190	1815	658	488	580	10.0	46
6	67.1	3.36	20.2	9.5	2740	1280	1950	655	425	545	20.0	50
9	64.1	3.20	19.2	13.6	3000	1430	1980	655	460	550	23.0	52
12	61.3	3.06	18.4	17.3	2910	1810	1960	610	495	530	24.0	55
15	58.7	2.94	17.6	20.7	2700	1560	1910	575	450	505	28.0	58
20	54.9	2.74	16.5	25.8	2650	1620	1290	560	438	375	30.0	62
25	51.5	2.58	15.5	30.4	2280	1660	1200	500	396	345	29.0	66
30	48.6	2.43	14.6	34.3	1910	1590	1280	460	304	305	27.0	69
40	43.7	2.18	13.1	41.1	1770	1390	1130	363	200	230	23.0	74

[1] Basic mix.

EFFECTS OF MAGNESIUM CARBONATE ALONE IN RUBBER

The data relating to the effect of magnesium carbonate on the physical properties of rubber are given in Tables I and II and represented graphically by the curves of Figs. 1 to 7, inclusive.

The behavior of magnesium carbonate, as shown in the stress-strain curves (Fig. 1), is seen to be that characteristic of a typical reinforcing pigment, as defined by Wiegand. With increasing volume additions of the pigment there is a very marked flattening of the curve, and when twenty volumes of the filler are present the curvature has practically disappeared and the stress-strain relationships are very nearly in accord with Hook's law for rigid materials, *i. e.*, proportionality of stress to deformation obtains. For certain proportions of the filler the tensile strength at rupture is increased above that of the basic mix, while at the same time the ultimate elongation is considerably decreased.

The tensile strength curve (Fig. 2) shows that this property of the rubber is increased up to a maximum at nine volumes of the filler per one hundred of rubber, and then falls off rather uniformly, becoming equal to that of the basic mix at about twenty volumes per one hundred of rubber (see Table I). Nine volumes of the carbonate correspond to about twenty-one parts by weight. With another lot of rubber, samples have been prepared containing twenty-five volumes of magnesium carbonate in which the tensile strength is equal to that of the basic mix. The curve for tensile strength after accelerated aging shows that this basic mix, containing an excess of litharge, does not stand up well under the heat test, whereas the heavily compounded samples, containing large proportions of magnesium carbonate and less rubber, age better than the lightly compounded ones. The curve for tensile strength after the 60-day weathering test is of a different character and practically parallels the curve for tensile properties before aging. Compounds containing between six and twelve volumes of magnesium carbonate show the highest tensiles after this aging test.

Ultimate elongation values for the stocks of the above series are represented in Fig. 3. The falling off on the elongation with increasing volume additions of magnesium carbonate is shown to be very nearly linear, up to forty volumes per one hundred of rubber (see Table I). After accelerated aging the decrease in elongation with increasing proportions of the filler is found to be uniform, though not linear, the elongation of every stock being considerably less than before aging, corresponding to the decrease in tensile which results from the application of this heat test. The 60-day weathering test gave quite different results. The lightly compounded samples retained after weathering the greater part of their original elongation, while the heavily compounded samples were much stiffer after this test than before. This difference in stiffness and hardness was observable to the eye, without carrying out tensile and elongation tests, and the heavily compounded samples also showed some surface checking and cracking, while those compounded with smaller proportions of magnesium carbonate did not.

Fig. 4 illustrates the effects of rubber compounding materials on the hardness of rubber, comparing light magnesium carbonate with gas black, zinc oxide, and ordinary ground magnesite, the last named being a coarse pulverized natural magnesium carbonate which is not a reinforcing pigment. Magnesium carbonate gives rubber hardness very much greater than that given by ground magnesite, somewhat greater than that given by zinc oxide, but considerably less than that given by gas black, which produces very hard and rigid compounds, even when used in rather small proportions (Table I). It appears, therefore, that there is a relationship between the hardness of rubber compounded with a particular filler and the reinforcing and toughening effect of that filler, which may perhaps be expressed in terms of the slope of the curve showing increase of hardness with successive volume increments of filler. This curve seems to be linear only for inert or coarse fillers, and not for reinforcing pigments.

The permanent set figures for rubber compounded with magnesium carbonate, in comparison with ground magnesite, zinc oxide, and gas black, are represented in Fig. 5. Magnesium carbonate shows a rapid increase in permanent set with successive volume increments, up to twenty volumes per one hundred of rubber, and then a uniform decrease from the maximum value (Table I). This decrease is explained by the fact that the ultimate elongation values for the heavily compounded stocks are small and, therefore, a 60 per cent extension of these samples is a much smaller actual stretch than in the cases of the more lightly compounded samples having higher elongation, and gives, therefore, a smaller result for the permanent set figure. Magnesium carbonate gives much greater set effects than either zinc oxide or gas black and greater still than ground magnesite. The latter gave no set figure higher than 12.0 per cent even up to fifty volumes of this filler. This, it appears, is due to the fact that even with smaller proportions of the material the set effect is not very great, and with larger proportions the great decrease in the final elongation corresponding to the diluent effect of this inert filler, permits low permanent set values to be obtained by this method of making the test.

High permanent set is an effect which seems to characterize in a degree all definitely crystalline substances which are used in compounding rubber, and the fact that magnesium carbonate particles have a definite crystal structure and acicular form is usually offered as the explanation of why magnesium carbonate gives high permanent set where other substances having approximately the same particle size do not show this effect. Zinc oxide, for example, although it possesses some of the properties of crystals, is amorphous in form and does not produce high permanent set. Let us consider the behavior of an individual crystal particle in rubber under stress, with particular regard to the internal structure of the vulcanizate. It may be assumed to start with that in freshly vulcanized rubber compounded with a substance such as magnesium carbonate, made up of small, definitely crystalline particles uniformly dispersed in the rubber, each particle is in complete and uniform contact with the rubber matrix, *i. e.*, the rubber adheres closely to each crystal face. The particles will lie with their axes at various angles to the direction of applied stress in the sample and when this stress is increased until the elongation is sufficiently great, say 60 per cent, as in the permanent set test discussed above, there will be a tendency for the particles to align themselves with their long axes in the direction of the applied stress. Very powerful shearing forces will then come into operation, acting between the plane surfaces of the crystal lying parallel to the direction of stress, and the rubber matrix to which each crystal face is united by cohesion forces. These surface forces vary with the physical and chemical nature of the crystalline substance to which the rubber is bonded, and probably also with the presence of other substances dispersed or dissolved in the rubber. When the bonding between the particles and the rubber has been broken and the filler particles have reoriented themselves in the mass, the rubber can never completely return to its original conformation and the individual particles will never reunite themselves to the rubber in the same degree as they were when the rubber was first vulcanized.

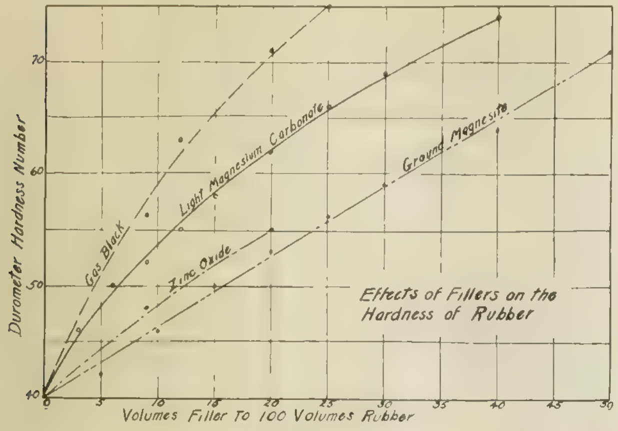

FIG. 4

Visible evidence of the separation of the magnesia particles from the rubber matrix may be obtained by stressing a sample cured with sulfur only. The sample will be practically translucent until blooming takes place, and when stretched there is a pronounced and permanent whitening, the result of the change in the refraction of the light passing through the rubber after the particles have become readjusted in the mass.

The behavior of an amorphous substance in rubber will be distinctly different, because the particles are irregular in surface contour and offer no plane surfaces to the rubber, which will, therefore, attach itself to the particle at many points of this irregular surface. The surface forces, therefore, instead of being exerted at plane surfaces and in one direction only, perpendicular to that surface, will be exerted in many directions, owing to the approximately spherical or irregular shape of the amorphous particle. Schippel[6] showed that compounded rubber when stressed gave an increase in volume, which he explained as being due to the formation of vacua at the poles of the particle in the direction of the applied stress. This was confirmed by Green,[7] who was able to show by examination of microsections of compounded rubber the actual formation of such vacua in rubber under strain, but his experiments indicated that no vacua were formed with fine pigments in rubber when compounded in small percentages. Wiegand[8] directed attention to the fact that when a stock containing one of the "active" fillers is stressed to rupture, a part of the energy required goes toward distorting the rubber phase itself and a considerable part toward tearing apart the rubber matrix and the imbedded pigment particles. In the case of an amorphous particle in rubber under stress there is only a slight separation of the rubber to form vacua at the poles and since no plane surfaces are subjected to shearing stresses, there is not such a pronounced tendency for the rubber matrix to break its bonding to the individual particles, entirely aside from specific cohesion forces exerted between the rubber and the particle surface. Consequently there will not be a great tendency for the particles to change their orientation in the mass and give a volume increase and high permanent set. The conclusion seems unavoidable, therefore, that an amorphous light magnesium carbonate would give less permanent set than is obtained with the crystalline material manufactured by the present process, and the modification of the precipitation process to produce a material of less pronounced crystalline characteristics and, if possible, even smaller particle size is being made the object of considerable study at the Mellon Institute of Industrial Research. If this can be accomplished it should make light magnesium carbonate of much greater value to the rubber compounder, and the writer hopes to have the privilege of presenting some results of the work along this line at the next meeting of the Rubber Division.

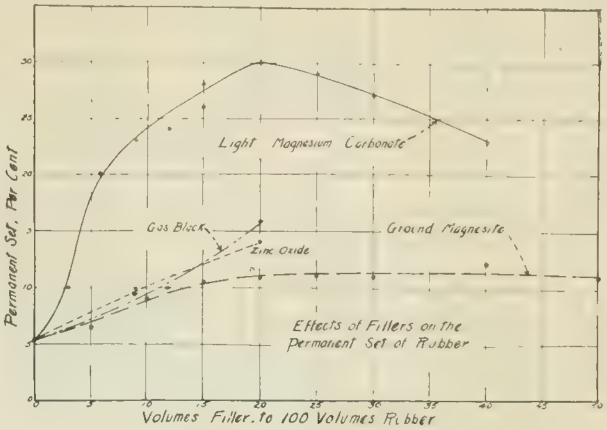

FIG. 5

Data representing the reinforcing effect of magnesium carbonate are shown in the tensile product and total resilient energy curves of Fig. 6. The tensile product values are not as high as those obtained by North, owing to the higher extensi-

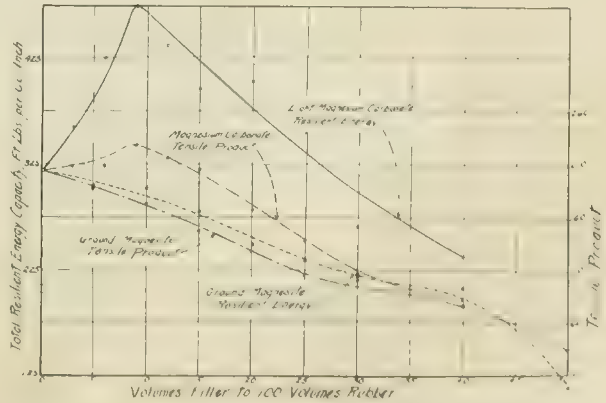

FIG. 6

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[6] THIS JOURNAL, 12 (1920), 33.

[7] *India Rubber World*, 65, (1922), 350.

THIS JOURNAL, 13 (1921), 118.

bility of the rubber-sulfur mix used in his work, as compared with that of this litharge-pale crepe mix. The curve has, however, approximately the same form. Tensile product reaches a maximum at nine volumes and becomes less than that of the basic mix at fifteen volumes; it is never very much greater than that of the basic mix. Quite different results are obtained with regard to resilient energy. (See Table II.)

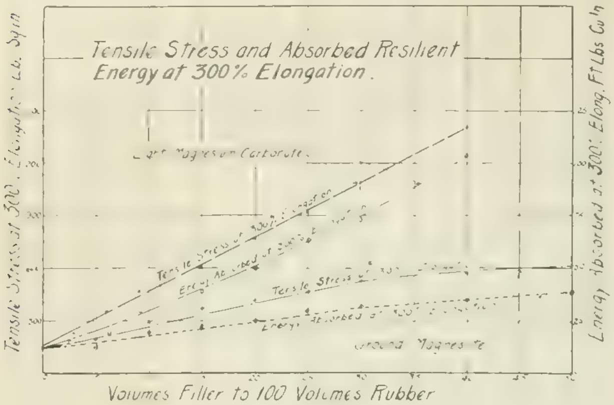

FIG. 7

TABLE II—DATA ON REINFORCING EFFECT OF LIGHT MAGNESIUM CARBONATE

Volumes Magnesium Carbonate to 100 Vol. Rubber	Tensile Product	Total Resilient Energy Ft. Lbs./Cu. In.	Resilient Energy Per cent of Base Mix Energy	Tensile Stress at 300 Per cent Elong. Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
0	205	318	100	150	11.7
3	205	355	112	225	16.7
6	208	425	134	355	20.5
9	227	475	149	455	31.7
12	212	438	138	505	35.0
15	197	396	124	600	39.0
20	174	407	128	770	50.0
25	137	355	112	910	63.4
30	107	265	83	1050	71.3
40	82	233	73	1405	104.0

The maximum is reached at nine volumes, the same maximum as for tensile strength and tensile product, and the total resilient energy is then 49 per cent greater than that of the basic mix. Resilient energy capacity of the compounds does not become less than that of the basic mix until more than twenty-five volumes of magnesium carbonate are incorporated.

For comparison purposes, the tensile product and total resilient energy curves for rubber compounded with various proportions of ground magnesite have also been plotted. The two curves are found to be almost identical in form, and the plotted values for tensile product and resilient energy decrease uniformly with each successive addition of this inert filler, being in every case less than the values for the basic mix. This illustrates the difference in mechanical qualities between rubber compounded with reinforcing pigments and with inert fillers. From a study of these curves the conclusion seems logical that for inert fillers either tensile product or resilient energy is a satisfactory index of the quality of the vulcanizate, but that for rubber compounded with "active" fillers resilient energy capacity gives a more accurate means of evaluation than does the tensile product, because tensile product measures only the actual stress at break, correcting for the decrease in the cross section of the test piece under stress, whereas resilient energy capacity takes into account the change in the character of the stress-strain curve, and it is this indication of the stress-strain relationships which determines the alteration in the physical properties of the product.

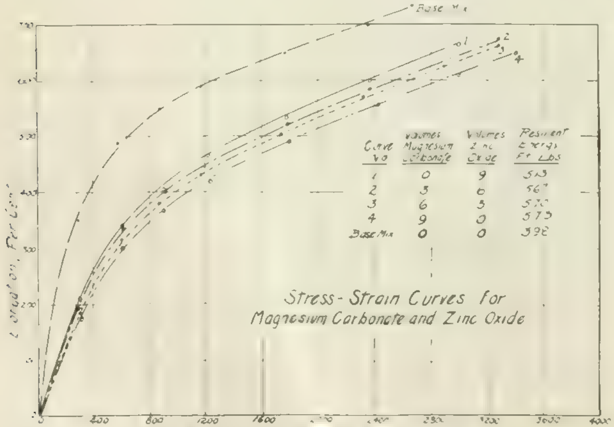

FIG. 8

W. W. Vogt[9] has directed our attention to the fact that if the tensile stress at 300 per cent elongation is plotted against the number of volumes of filler per one hundred volumes of rubber, the curve obtained is linear, showing an increase in load with increasing amounts of filler. The slope of this line, he concludes, is a measure of the stiffening or reinforcing action of the filler. On Fig. 7 will be found curves showing the relation between tensile stress at 300 per cent elongation for magnesium carbonate and for ground magnesite. The magnesium carbonate curve has a much greater slope than the ground magnesite curve, which is to be expected, corresponding to its greater reinforcing action. The slope of this line indicates the *rate of flattening* of the fore part of the stress-strain curve with increasing volume additions of the filler which is being studied. The magnesium carbonate curve is linear throughout and the ground magnesite curve is linear up to thirty volumes, and then flattens out somewhat.

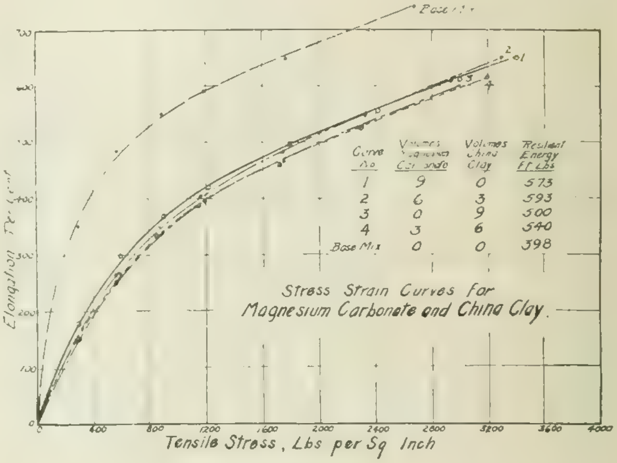

FIG. 9

On the same graph, for comparison purposes, there have been plotted the values for the resilient energy absorbed at 300 per cent elongation by rubber compounded with various proportions of light magnesium carbonate, and also with ground magnesite. The curves for absorbed energy at 300 per cent elongation are very similar in form to those just discussed above for tensile stress at 300 per cent elongation, although they are not perfectly linear. The spread between the absorbed energy curves for magnesium carbonate and ground magnesite is almost identical with that between the curves for tensile stress at 300 per cent elongation for the same fillers, and since the energy capacity of the rubber at 300 per cent elongation also depends upon the flattening of the fore part of the curve, the slope of the line

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[9] *India Rubber World*, **65** (1922), 347.

Table III—Data on Mixtures of Light Magnesium Carbonate with Other Reinforcing Pigments

Volumes Filler to 100 Volumes Rubber										
Magnesium Carbonate	Gas Black	Zinc Oxide	China Clay	Colloidal Barium Sulfate	Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Permanent Set Per cent	Durometer Hardness Number
0[1]	0	0	0	0	2650	1200	738	550	6.0	42
9	0	0	0	0	3400	2275	650	550	19.5	51
6	3	0	0	0	3440	2070	638	505	17.0	52
3	6	0	0	0	3600	1710	635	380	16.5	54
0	9	0	0	0	3450	1190	600	345	9.5	53
6	0	3	0	0	3290	2290	665	610	15.0	50
3	0	6	0	0	3285	2410	675	570	12.0	50
0	0	9	0	0	3000	1760	665	600	10.5	49
6	0	0	3	0	3300	2060	653	550	18.5	50
3	0	0	6	0	3200	2080	615	525	17.5	50
0	0	0	9	0	3000	1780	600	485	16.0	49
6	0	0	0	3	3075	2040	677	580	13.5	50
3	0	0	0	6	3020	1760	653	540	12.0	49
0	0	0	0	9	2810	1650	700	500	9.0	44

[1] Basic mix.

showing the change in this quantity with successive increments of filler also measures the *rate of flattening* of the lower portion of the curve and may properly be considered an index of the reinforcing action of the pigment whose effect is being investigated. This would enable the investigator to make a direct comparison between the reinforcing effects of different pigments on the basis of energy relationships rather than on tensile stress alone.

Comparison of Magnesium Carbonate with Other Reinforcing Pigments

Light magnesium carbonate gives its maximum reinforcing effect with respect to tensile strength, tensile product, and resilient energy capacity at nine volumes per one hundred of rubber. Magnesium carbonate was therefore compared at this volume ratio with equal proportions by volume of zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. The effects of mixtures of magnesium carbonate with each of these fillers upon the physical properties were also studied, having a total of nine volumes filler in each compound, and varying by three-volume increments the proportions of magnesium carbonate and the other reinforcing pigments. These data, as given in Tables III and IV, and Figs. 8 to 18, inclusive, show in graphic form the changes in physical properties. It must be understood, of course, that nine volumes of the pigments other than magnesium carbonate do not represent the point of maximum reinforcement, which in the case of gas black, for example, is not reached until about twenty volumes are incorporated.

In Fig. 8 are represented the stress-strain curves for mixtures of magnesium carbonate and zinc oxide. Magnesium carbonate is shown to give a greater stiffening effect than zinc oxide in this volume ratio. The stress-strain curves of Fig. 9 for mixtures of magnesium carbonate and china clay show that magnesium carbonate has a stiffening action which is very slightly less than that of china clay. Fig. 10 gives stress-strain curves for similar mixtures of magnesium carbonate with colloidal barium sulfate, which show that magnesium carbonate has a much greater reinforcing and stiffening action than colloidal barium sulfate. Stress-strain curves for mixtures of magnesium carbonate and gas black are represented in Fig. 11. These show that gas black gives a stiffer rubber than magnesium carbonate, and that it has also a greater reinforcing action than china clay. In every case the mixtures of magnesium carbonate with the other reinforcing pigments give reinforcing effects intermediate between those obtained with either material in the same volume ratio alone, as shown by the relative positions of their stress-strain curves.

Tensile strength data for the compounds just discussed, represented by the curves of Fig. 12, show that magnesium carbonate compounded in the nine-volume ratio produces tensile strength somewhat greater than that given by zinc oxide or china clay in equal proportions, and considerably greater than that given by colloidal barium sulfate. The tensile with nine volumes magnesium carbonate is slightly less than that produced by nine volumes of gas black. The curve shows, and this has been confirmed by the preparation of several samples, that a mixture of six volumes gas black and three volumes magnesium carbonate per one hundred volumes of rubber gives a tensile value of 3600 lbs. per sq. in., considerably higher than can be obtained by the use of the same total volume of either filler alone in this basic mix. With the other reinforcing pigments, zinc oxide, china clay, and colloidal barium sulfate, there is a uniform falling off in tensile strength, with successive replacements of magnesium carbonate in the compound, by any one of these fillers (see data in Table III).

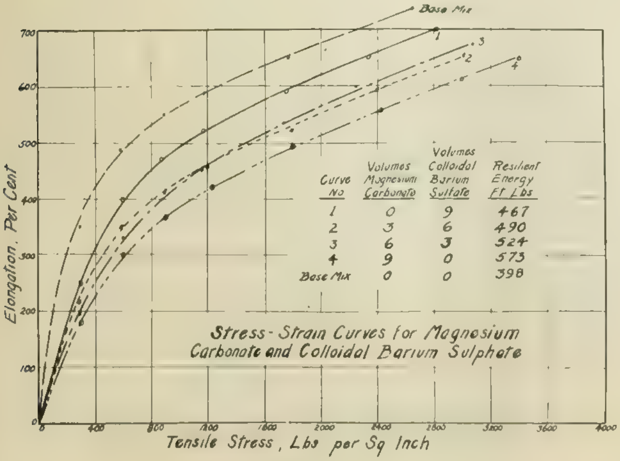

Fig. 10

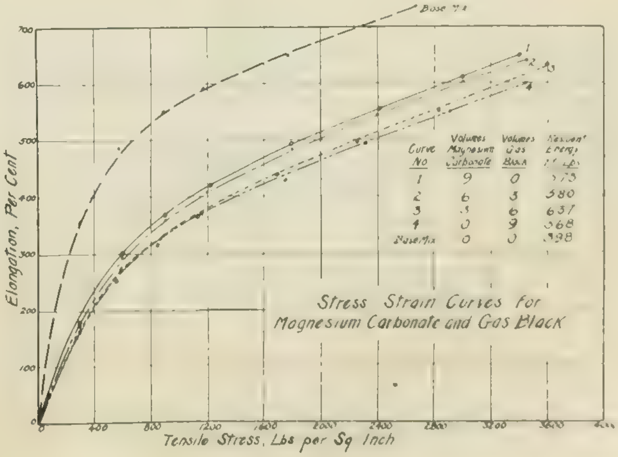

Fig 11

Fig. 13 shows the loss in tensile strength of these compounds resulting from the accelerated aging test (data given in Table III). Inspection of the curves makes it evident that in this basic mix stocks containing gas black do not stand up well under this heat test. The best aging samples are those compounded with mixtures of zinc oxide and magnesium carbonate, although the stock containing zinc oxide alone loses a greater proportion of its original tensile strength. Samples compounded with colloidal barium sulfate, with china clay, with gas black, and with mixtures of magnesium carbonate with these other materials show poorer tensile values after accelerated aging than was the case with the compound containing only magnesium carbonate. In so far as this test may be considered of value in determining the aging qualities of compounded rubber, it is evident that magnesium carbonate compares very favorably with these other reinforcing pigments. The magnesium carbonate sample has lost 33 per cent of its original tensile strength, while the other compounding materials show losses of from 41 to 65 per cent.

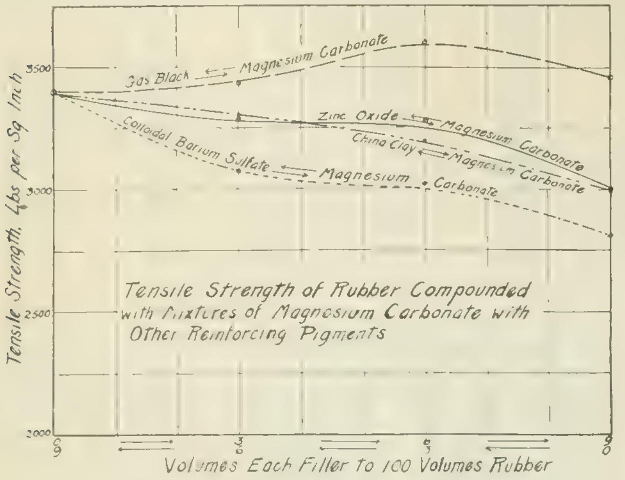

FIG. 12

The hardness of rubber compounded with mixtures of magnesium carbonate and these reinforcing pigments is shown by the curves in Fig. 14 (see data in Table III). In this volume ratio magnesium carbonate gives a vulcanizate slightly harder than is produced by the same proportion of either zinc oxide or china clay, and considerably harder than that given by the same volume of colloidal barium sulfate. This same volume of gas black gives a compound which is quite definitely harder than the magnesium carbonate compound.

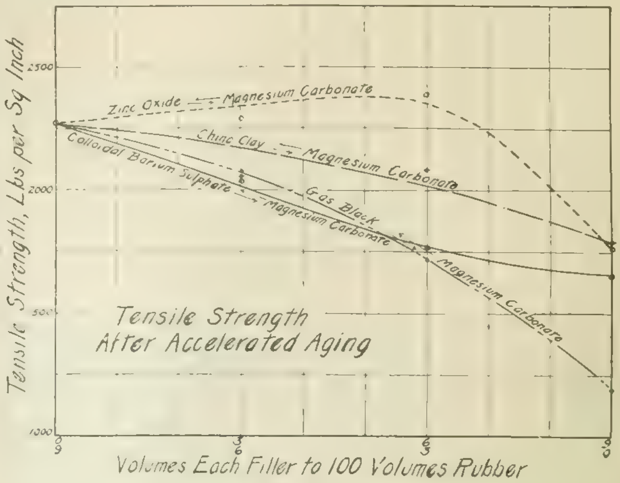

FIG. 13

Fig. 15 shows just the sort of results with respect to permanent set with mixtures of magnesium carbonate and other reinforcing pigments which would be anticipated from the preceding data and discussion of the permanent set effect given by magnesium carbonate, since these other fillers are all more amorphous than the carbonate. The set with mixtures of china clay and magnesium carbonate increases almost linearly with increasing proportions of magnesium carbonate, although clay itself produces rather high permanent set. In the case of mixtures of gas black and magnesium carbonate the set increases more rapidly than in a linear ratio. The permanent set of the compound previously referred to, containing six volumes gas black and three of magnesium carbonate, is 17.5 per cent. It should be remarked that the compound containing nine volumes of carbonate, although it has a greater tensile strength than was given by the same volume of this filler in the other lot of pale crepe used in the preliminary study of its effect, gives a lower permanent set, only 19.5 per cent, as compared with 23.0 per cent.

The rate of increase in permanent set in the compounds containing mixtures of magnesium carbonate with zinc oxide and with colloidal barium sulfate is seen to be less than that corresponding to a linear ratio.

The resilient energy capacity curves, Fig. 16, show some interesting results. Magnesium carbonate shows higher resilient energy in this volume ratio than zinc oxide, china clay,

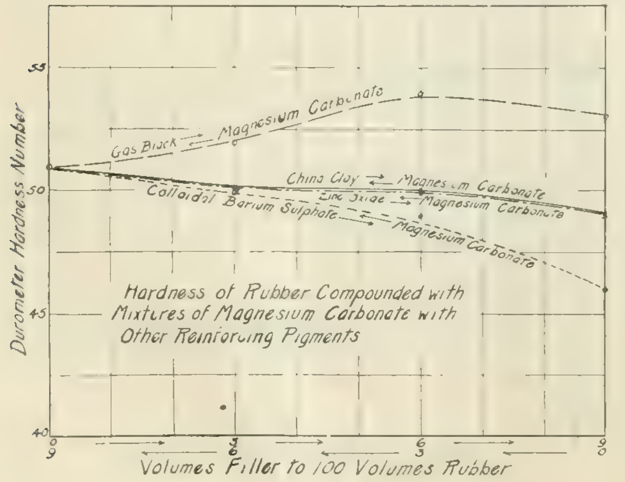

FIG. 14

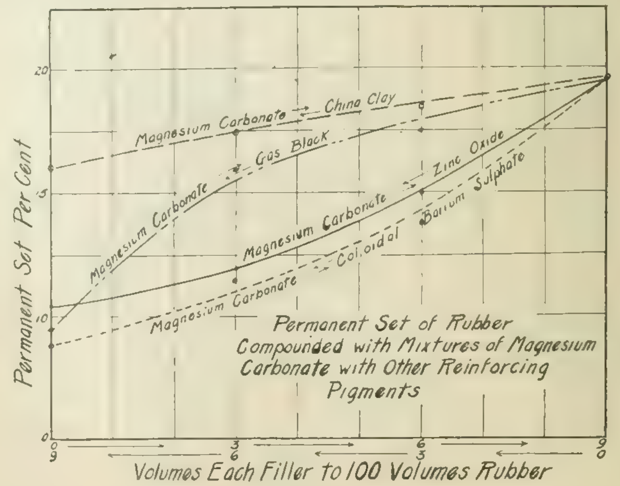

FIG. 15

Table IV—Data on Reinforcing Effects of Mixtures of Magnesium Carbonate and Other Reinforcing Fillers

Volumes Filler to 100 Volumes Rubber: Light Magnesium Carbonate	Gas Black	Zinc Oxide	China Clay	Colloidal Barum Sulfate	Tensile Product	Total Resilient Energy Capacity Ft. Lbs./Cu In.	Resilient Energy Per cent of Basic Mix Energy	Tensile Stress at 300 Per cent Elongation Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
0[1]	0	0	0	0	222	398	100	200	25
9	0	0	0	0	255	573	144	600	68
6	3	0	0	0	253	580	146	650	70
3	6	0	0	0	265	637	160	715	77
0	9	0	0	0	242	568	142	775	80
6	0	3	0	0	252	570	143	565	62
3	0	6	0	0	255	567	142	525	57
0	0	9	0	0	230	513	129	490	52
6	0	0	3	0	248	593	149	650	73
3	0	0	6	0	228	540	136	700	71
0	0	0	9	0	210	500	126	745	79
6	0	0	0	3	239	524	132	515	57
3	0	0	0	6	228	490	123	465	50
0	0	0	0	9	225	467	117	380	44

[1] Basic mix.

Table V—Data on Mixtures of Light Magnesium Carbonate with Zinc Oxide

Volumes Filler to 100 Volumes Rubber: Light Magnesium Carbonate	Zinc Oxide	Gas Black	Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Tensile after 60-Day Weathering Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Ult. Elong. after 60-Day Weathering Per cent	Permanent Set Per cent	Durometer Hardness Number
0[1]	0	0	2650	1200	1780	738	562	530	6.0	42
20	0	0	2890	1720	1290	560	460	413	28.0	64
15	5	0	2950	1720	1270	580	415	425	24.0	60
11	9	0	2830	1860	1540	585	463	494	15.0	58
7	13	0	2780	1730	1730	600	448	522	14.0	57
3	17	0	2840	1890	1970	595	500	535	16.0	56
0	20	0	2820	1760	1870	615	520	545	12.0	55
0	0	20	3950	1580	..	490	230	..	16.5	70

[1] Basic mix.

or colloidal barium sulfate, and equal to that of gas black. The high resilient energy values obtained with this proportion of magnesium carbonate are explained by the fact that this material gives high tensile strength, high elongation, and a pronounced flattening of the stress-strain curve; therefore the area between the curve and the elongation axis is large and the calculated resilient energy is correspondingly great. The compound previously noted, containing six volumes gas black and three of magnesium carbonate, which gives high tensile strength, is also found to give the highest resilient energy value, 637 ft. lbs., or 60 per cent increase above the energy of the basic mix (see data in Table IV).

A comparison of the stiffening effect produced by magnesium carbonate and the other reinforcing pigments studied, on the basis of tensile stress at 300 per cent elongation, is given in Fig. 17 (based on data in Table IV). The curves representing tensile stress at 300 per cent elongation are all linear, for these mixtures of reinforcing pigments, and with respect to stiffening effect at this volume ratio of each filler, would place them in the following order of increasing reinforcing power: colloidal barium sulfate, zinc oxide, magnesium carbonate, china clay, gas black.

Fig. 18 gives curves for energy absorbed at 300 per cent elongation, making possible a direct comparison of these mixtures of magnesium carbonate with other reinforcing pigments, on the basis of energy values rather than on tensiles alone. The curves, it will be seen, lie in about the same relative positions and have approximately the same spread,

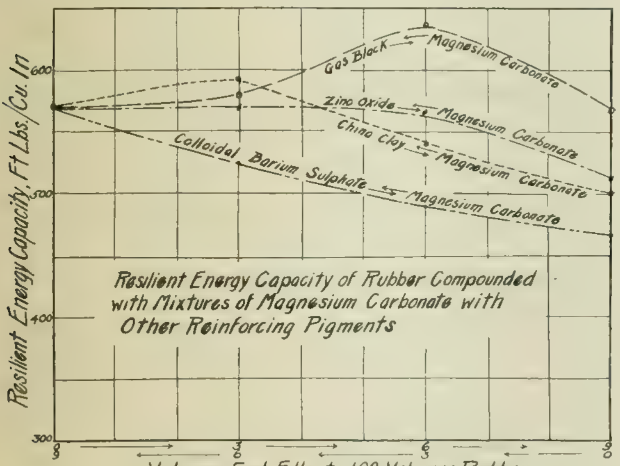

Fig. 16

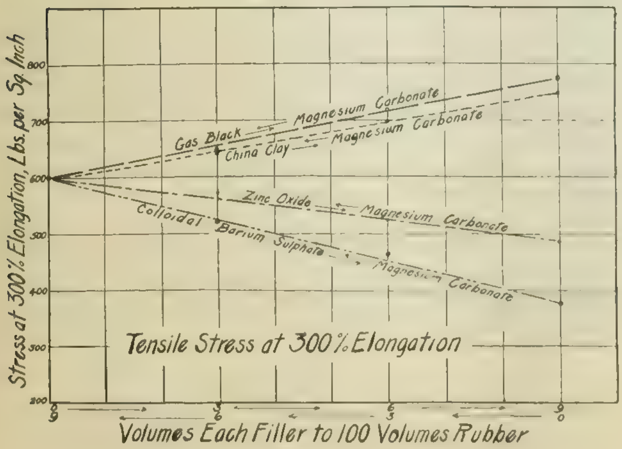

Fig. 17

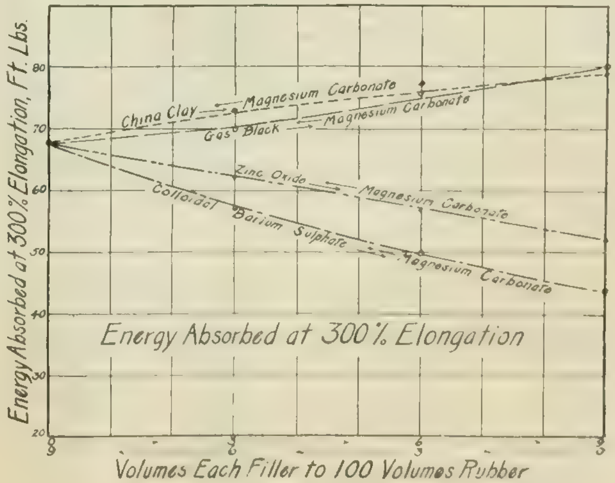

Fig. 18

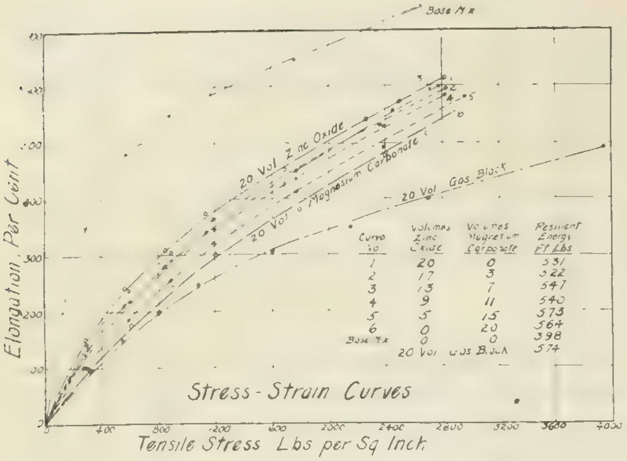

FIG. 19

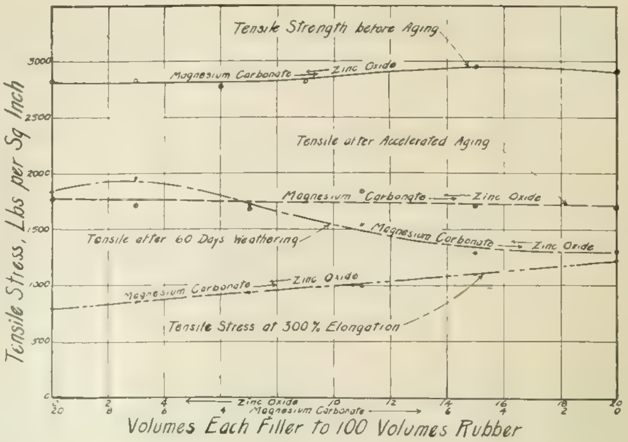

FIG. 20

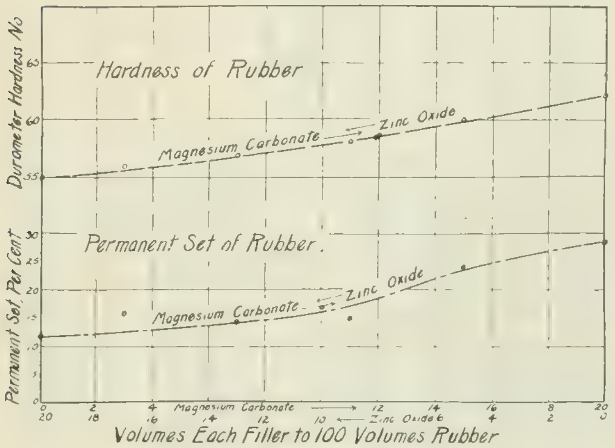

FIG. 21

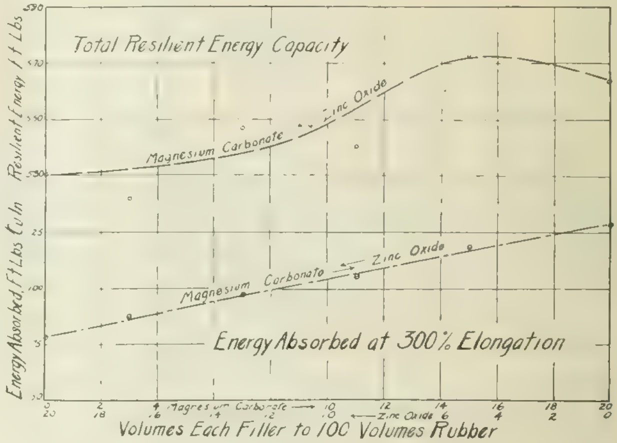

FIG. 22

but are not exactly linear. The order of increasing reinforcing power in the rubber is the same as given above for tensile stress at 300 per cent elongation, except that gas black and china clay are more nearly equal. (See Table IV.) It should be remarked, however, that this comparison takes into account only the stiffening effect on the fore part of the stress-strain curve and does not express the fact that higher tensile strength and total energy values are given by gas black and magnesium carbonate than can be obtained with clay. Schidrowitz and Burnand[10] have pointed out, also, that great rigidity is not always associated with toughness (especially in the case of overcured samples) although this might be thought to be the case simply from a study of the stress-strain curves. Total resilient energy, however, takes into account both tensile strength and ultimate elongation in evaluating the physical properties, because for compounds, the lower portions of whose stress-strain curves are identical, the one which has the greatest tensile and elongation values will also give the greatest calculated resilient energy.

REINFORCING EFFECTS OF ZINC OXIDE AND MAGNESIUM CARBONATE AT TWENTY VOLUMES

The comparative study of magnesium carbonate and zinc oxide in more heavily compounded stocks, containing a total of twenty volumes filler, the data for which are given in Tables V and VI, and represented by the curves in Figs. 19 to 22, inclusive, confirms completely the results just discussed with regard to the reinforcing effect of magnesium carbonate in the nine-volume ratio.

The stress-strain curves, Fig. 19 (see Table V for data), show considerably greater stiffness for magnesium carbonate and for the compounds containing mixtures of zinc oxide with magnesium carbonate than for zinc oxide alone. There is a uniform decrease in ultimate elongation with increasing proportions of magnesium carbonate. For comparison purposes the stress-strain curve for twenty volumes gas black has also been plotted and is found to represent a much more rigid compound and one of higher tensile strength and lower ultimate elongation than is obtained by using equal volumes of either zinc oxide or magnesium carbonate.

TABLE VI—DATA ON REINFORCING EFFECTS OF MIXTURES OF LIGHT MAGNESIUM CARBONATE WITH ZINC OXIDE

Volumes Filler to 100 Volumes Rubber							
Light Magnesium Carbonate	Zinc Oxide	Gas Black	Tensile Product	Total Resilient Energy Capacity Ft. Lbs./Cu. In.	Resilient Energy Per cent of Basic Mix Energy	Tensile Stress at 300 Per cent Elongation Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
0[1]	0	0	222	398	100	200	25.0
20	0	0	191	564	142	1230	128
15	5	0	200	573	144	1150	113
11	9	0	194	540	136	1040	100
7	13	0	195	547	137	980	95
3	17	0	197	522	131	860	88
0	20	0	202	531	133	810	77
0	0	20	194	574	144	1520	155

[1] Basic mix.

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[10] *J. Soc. Chem. Ind.*, 40 (1922), 268*t*.

The tensile strength curves, Fig. 20, show values for this property which are nearly the same for all the compounds, probably within the experimental error due to slight differences in the state of cure. The same is true of the tensile values after accelerated aging. After the 60-day weathering test, however, it is observed that the stocks containing the larger proportions of zinc oxide show definitely better aging qualities than those containing larger proportions of magnesium carbonate, as a result of the greater surface cracking tendency of rubber heavily compounded with magnesium carbonate. This again seems to be related in a degree to the crystalline character of the magnesium carbonate particles, since the plane surfaces and sharp edges of the crystals would be expected to favor the development of cleavage planes in the rubber itself when stressed, or perhaps even under the influence of changes in temperature, producing alternate expansion and contraction of the rubber matrix around each particle.

The hardness and permanent set (Fig. 21) of these compounds both show increasing values with increasing proportions of magnesium carbonate. The permanent set, however, does not exceed 16 per cent until half the zinc oxide has been replaced by magnesium carbonate.

The total resilient energy capacity and energy absorbed at 300 per cent elongation (Fig. 22 based on data in Table VI) both show a marked increase with successive increments of magnesium carbonate replacing zinc oxide in the compound. For the absorbed energy at 300 per cent elongation this increase is linear, as is also true of the curve showing stress at 300 per cent elongation for the same compounds (Fig. 20).

The Application of Ion Concentration Measurements to the Control of Industrial Processes[1]

By Earl A. Keeler[2]

Leeds & Northrup Co., Philadelphia, Pennsylvania

The significance of ion concentrations has been the subject of many investigations during the last few years. The results obtained have demonstrated without question the unlimited possibilities existing for laboratory and industrial application of ion concentration measurements. It has been shown that in many instances biological activity, fermentation, and filtration are influenced to a large extent by variations in the H-ion concentration, or reaction of the solutions involved. In addition, the way is open for improved control and accuracy in the many neutralization problems encountered in industrial chemical processes. Automatic control by means of motor driven valves and regulating apparatus has become a reality, and it is safe to predict that many troublesome problems of the present time will soon be handled automatically with great saving of labor and expense.

The most widely known and most important of ion concentration measurements is that of the hydrogen ion. Many reactions occurring in colored or opaque solutions cannot be adequately governed by the use of color indicator. Quite frequently the hydrogen electrode is used to secure results that are impossible with the use of indicators. Another important asset lies in the ability of the hydrogen electrode to distinguish between actual acidity and total acidity. The controlling factor in reactions is usually the actual acidity, which depends directly upon the H-ion concentration. Total acidity, as determined by titration, is a measurement of quantity or available acidity, and its effect upon reaction is indirect. An excellent example of the errors that one may be led into by depending upon total acidity measurement is found in the test of milk by titration with standard alkali. Milk of good quality, but containing a relatively large amount of acid salts, has often been rejected because of a high acidity as determined by titration. Another batch of milk of equal quality but containing less salts will exhibit a lower acidity when titrated. The actual acidity is largely due to the lactic acid content and can be measured by the H-ion concentration.

In the past, the lack of suitable electrodes has greatly retarded the practical applications of H-ion measurements to plant industrial problems. Fig. 1 shows a typical laboratory set-up consisting of a hydrogen electrode and a calomel electrode connected into a potentiometer circuit. One can readily realize the difficulties that would be encountered in applying such structures, or even radical modifications, to plant work. The calomel electrode at its best has often been a troublesome affair for unskilled hands to handle, and the hydrogen electrodes have lacked the requirement of convenient and rapid change of electrode surfaces. Contamination of hydrogen electrodes is usually unavoidable in most industrial processes. For this reason it is extremely important that the electrode elements may be easily removed and replaced.

Several new electrodes which are well suited for industrial work have been recently developed. These electrodes are shown in section in Fig. 2. It is to be noted that the structures are practically unbreakable, there being no glass parts used. The hydrogen electrode element is a disk of platinum gauze held in position by a knurled ring of hard rubber. A fresh electrode disk may be substituted for a used disk inside

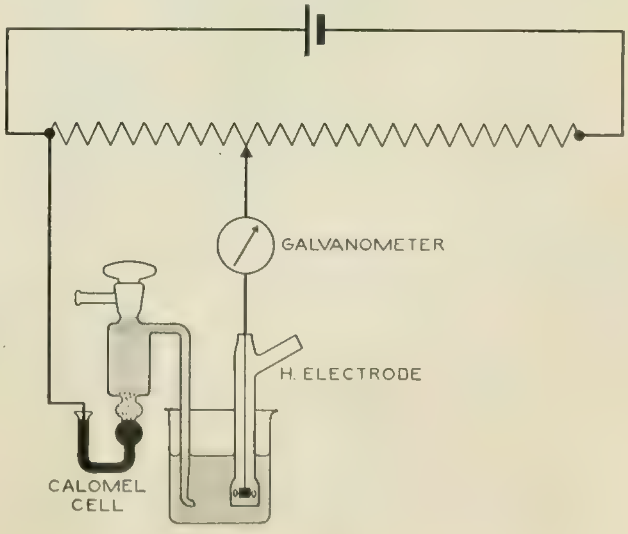

Fig. 1

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[1] Received February 24, 1922.

[2] Research Engineer, Leeds & Northrup Co.

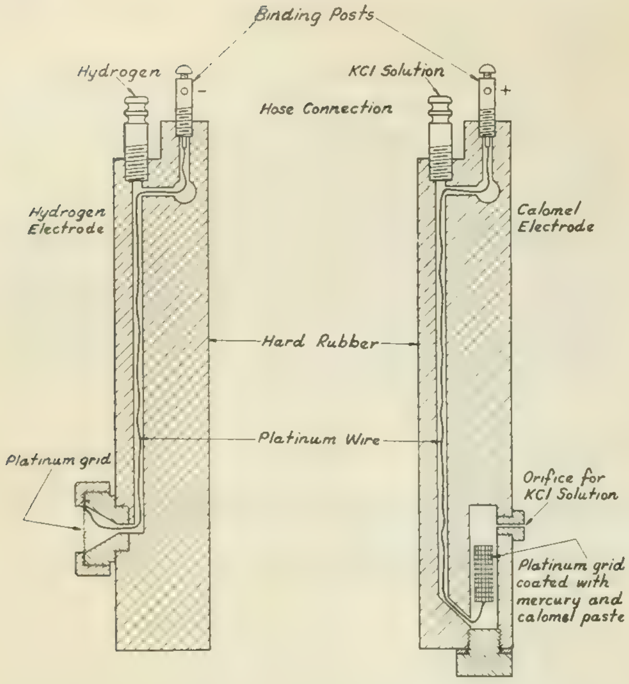

Fig. 2

of one minute. The calomel electrode is also unbreakable and contains no loose mercury. By coating a platinum grid with a paste of mercury and calomel, an electrode is secured that can be shipped ready for use. The only requirement is that a reservoir of potassium chloride solution be connected to supply the small flow of potassium chloride necessary to prevent diffusion of the solution under test into the calomel electrode. Fig. 3 shows the electrodes of Fig. 2 combined into one structure. The terminals, or binding posts, are shown at E and F. G and H are the connections for hydrogen and the potassium chloride solution. The knurled ring holding the hydrogen electrode disk is shown at B. The orifice of the calomel electrode is the removable plug C. The knurled end plug D closes the calomel electrode chamber into which the paste-coated grid is mounted. The main body of the combined electrode, A, is made of hard rubber.

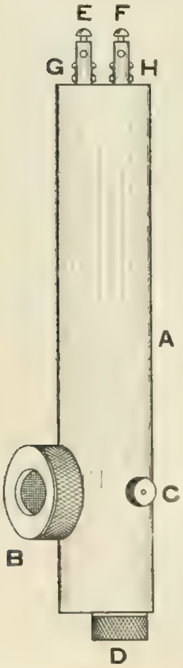

Fig. 3

Another form which the electrode structure may take is shown in Fig. 4. Here a radical departure has been made from the usual method of applying the hydrogen gas to the electrode. Instead of bubbling the gas into the solution around the electrode, the flow of solution through a small aspirator is made to entrain the gas and direct it against the electrode disk. In this manner the gas is broken up into minute bubbles and distributed through the solution. Such an electrode has been found very satisfactory for continuous flow applications, such as the recording and control of boiler feed water acidity. A small glass wool filter connected as in Fig. 4 will greatly increase the period over which an electrode disk may be used before removal for cleaning and replatinizing is necessary. A change of the hydrogen electrode disks every two or three days is advisable, although experience has shown that such electrode will sometimes operate satisfactorily for several weeks without cleaning.

The hydrogen-ion method is particularly well adapted to the control of neutralization processes and the measurement of low acidity or alkalinity. Fig. 5 shows a reproduction of a record produced by an automatic hydrogen-ion recorder during the reaction of sodium hydroxide solution with hydrochloric acid solution. It will be noted that the greatest change of voltage for a given change in acidity takes place around the neutral point. The ordinate of this record is marked "time" and may be taken as proportional to change of acidity or alkalinity. The records shown in Figs. 6, 7, 8, 9, and 10 are typical of the results that are secured upon application of the hydrogen-ion recorder to many industrial problems.

The carbonation of beetsugar juice is shown in the record of Fig. 6. Milk of lime had been added to this juice prior to the carbonation. It will be noted that the curve is practically flat (1.05 volts) during the first portion of the carbonation. Then a break occurs, producing a "knee" in the curve. During the remainder of the carbonation the slope of the curve is very appreciable, thus giving considerable change in voltage for small changes in alkalinity. Three samples were taken between the "knee" of the curve and the neutral point. The titration of these samples was made with 0.036 N sulfuric acid and the results expressed in grains of calcium oxide per 100 cc. of solution. Phenolphthalein was used as an indicator.

Fig. 7 shows the record secured during the neutralization of pineapple juice. Milk of lime is added to the juice until the neutral point is reached. Phenolphthalein tests showed that 0.75 volt corresponded to the real neutral point.

An interesting application of the recorder is shown in Fig. 8. The changes of alkalinity occurring when tooth paste goes into water solution are of importance because of the necessity for proper neutralization of the reaction known as "acid

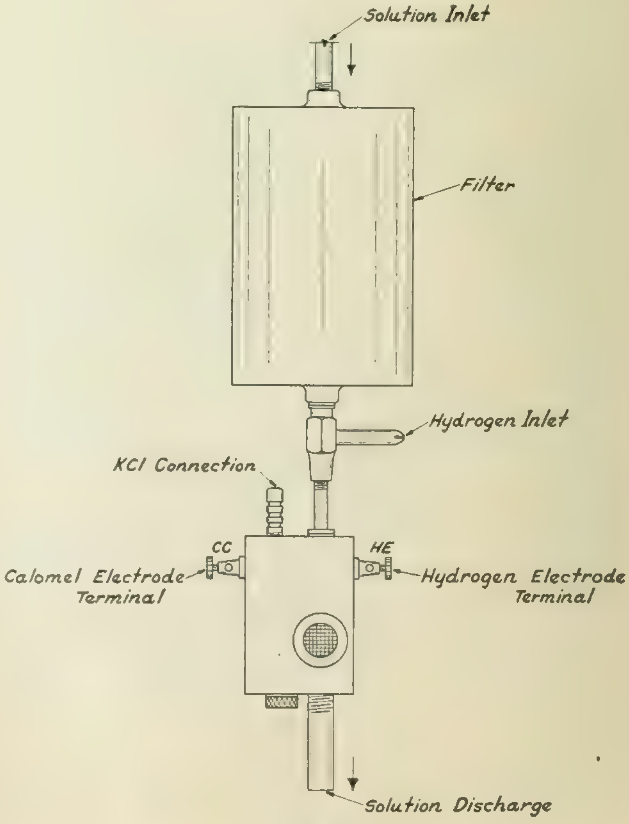

Fig. 4

mouth." The shape of the curve shows that the alkalinity becomes practically constant after the first 2 or 3 minutes.

A peculiar record is reproduced in Fig. 9. The alkalinity of wool scouring liquor is difficult to determine because of the color and suspended matter of all kinds. A titration of some of this liquor with sulfuric acid resulted in the record of Fig. 9. The liquor contains some free alkali in the form of soda ash, some soap made up of red oil, soda ash, and the solution constituents of the greasy wool containing complex organic acids combined with potash. It seems that there are three steps involved in the neutralization: (1) the neutralization of the free alkali; (2) the decomposition of the red oil soaps; and (3) the liberation of a gas caused by the decomposition of the potash-organic acid compounds.

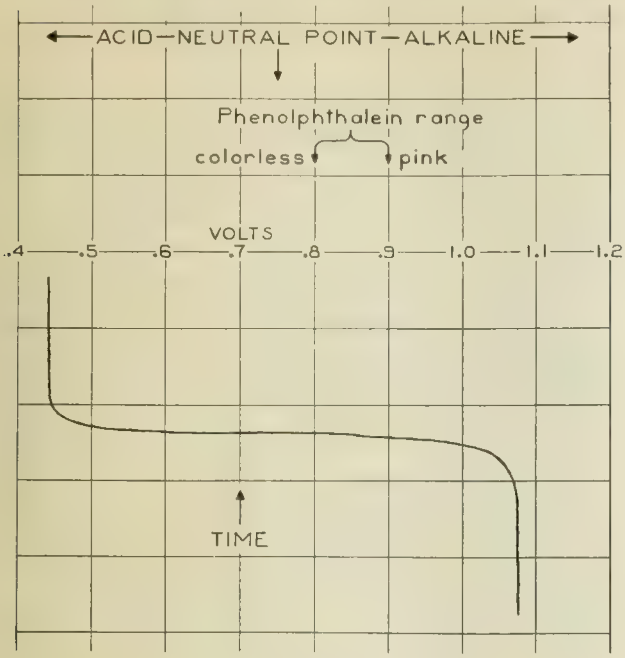

FIG. 5

Another interesting feature is shown in Fig. 10, and here the two end-points of the reaction of phosphoric acid with sodium hydroxide indicate the formation of the primary and secondary phosphates.

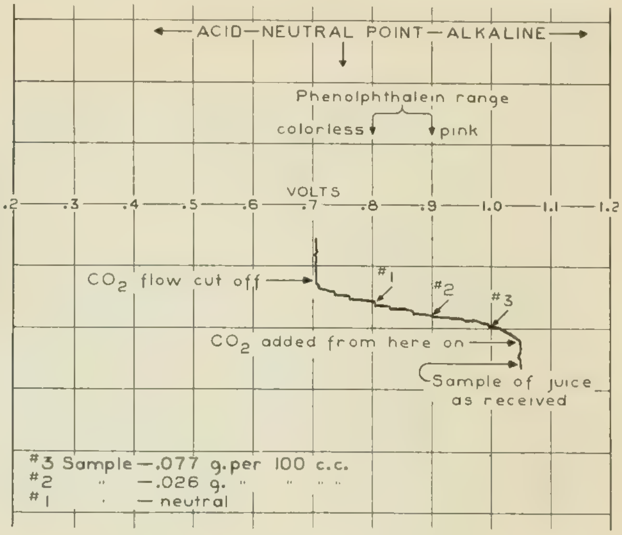

FIG. 6

These are only representative of the many possibilities existing for the application of ion concentration methods. Several comprehensive papers have recently been published on the subject of H-ion measurements as applied to filtration problems in water purification[3] and sewage disposal.[4] Another subject upon which a great deal of interesting work has been done, is that concerning the effect of the hydrogen-ion concentration upon the properties of tanning liquors used in the leather industry.[5]

The step from recording apparatus, such as that shown in Fig. 11, to equipment for automatic control is a natural one to undertake. Frequently, the advantages to be gained by automatic control are far greater than those secured by re-

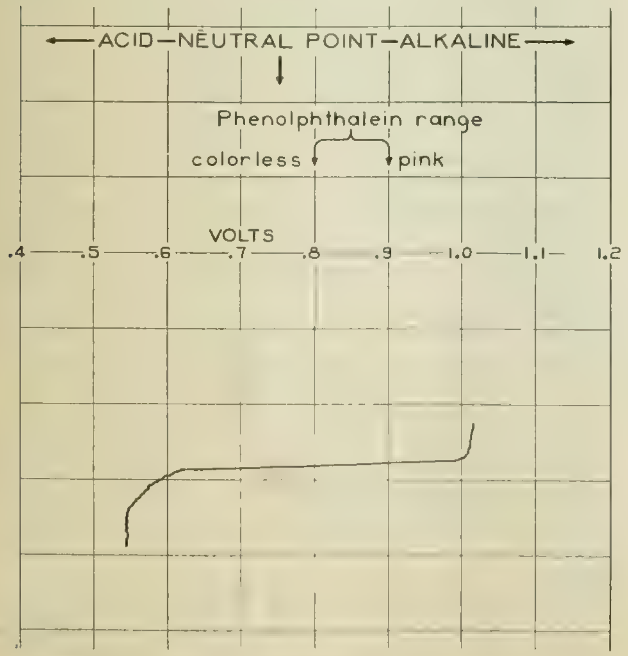

FIG. 7

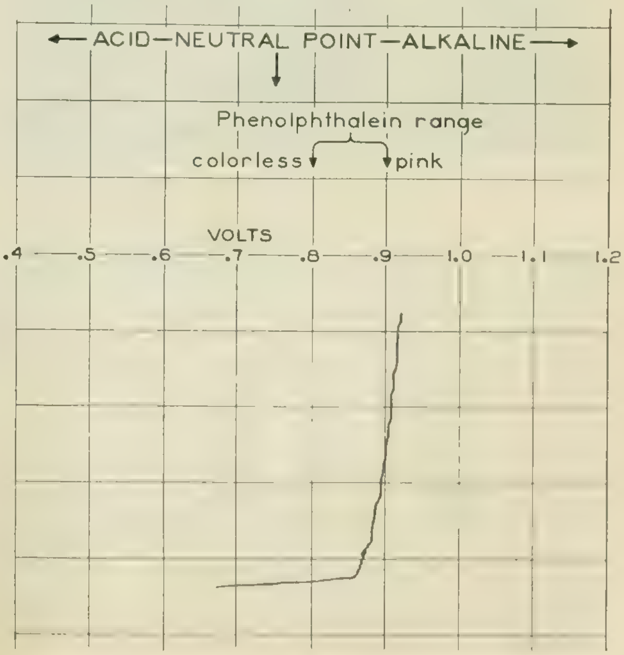

FIG. 8

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[3] Abel Wolmand and Frank Harman, *Chem. Met. Eng.*, **25** (1921), 502.

[4] J. A. Wilson and H. M. Heisig, THIS JOURNAL, **13** (1921), 406.

[5] J. A. Wilson and Erwin J. Kern, *Ibid.*, **13** (1921), 1025.

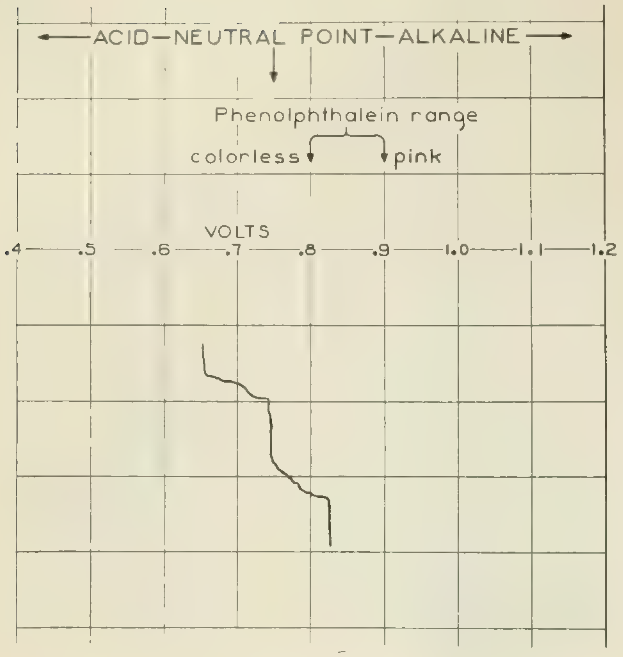

Fig. 9

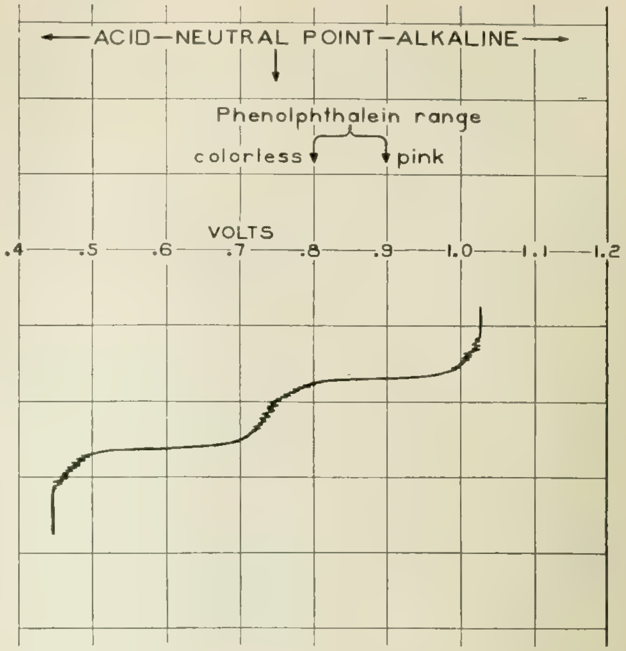

Fig. 10

cording alone. An illustration of such a condition is found in the requirements for efficient operation of boilers in a modern power plant. It is known that the hydrogen-ion concentration, or actual acidity of boiler feed, is one of the factors upon which the corrosion of a steam boiler and its auxiliaries depends. Maintenance of feed water at a slight alkalinity usually reduces corrosion to a minimum. An installation consisting of a hydrogen-ion recorder equipped with control contacts, aspirator electrodes, and an automatic valve for controlling additions of alkalinity to boiler feed is now in operation. Work on other control problems is rapidly progressing, and it is expected that the experience gained will facilitate the further application of hydrogen-ion control methods to many industrial problems.

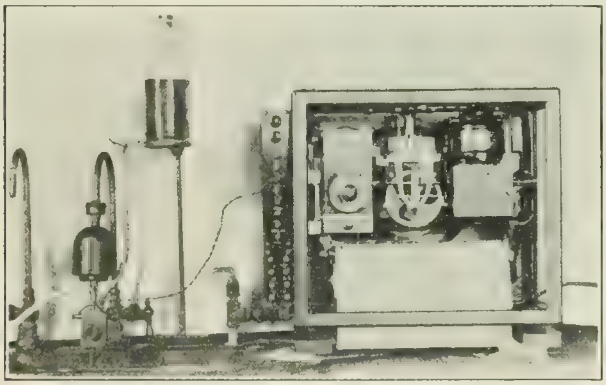

Fig. 11

In order to promote original research relative to the fungicidal and insecticidal properties of sulfur and the effects of sunlight, temperature and moisture on its action, the Crop Protection Institute expects to offer two fellowships yielding an income of $2500 each. Training in chemistry and plant physiology is a prerequisite, and candidates should have demonstrated ability to undertake research efforts of a high type. A statement explaining the purposes and scope of the projects and selection of research laboratory may be obtained from the Crop Protection Institute, National Research Council, Washington, D. C.

Civil Service Examinations

The United States Civil Service Commission has announced an examination for associate chemist at $2500 to $3600 a year and assistant chemist at $1800 to $2500 a year, applications to be rated as received until further notice. Applicants must qualify in one of the following branches of chemistry: advanced inorganic, analytical, biological, dairy, explosives, food, fuel, metallurgical, organic, pharmaceutical, physical, soil, petroleum, gas, ceramic. Applicants will be rated on education, training and experience—70 points, publications or thesis (to be filed with application)—30 points. While applications for examination in all of the fifteen optional subjects are desired, there is particular need for eligibles qualified in the chemistry of explosives.

An examination has also been announced for junior wharf examiner (food and drugs), to take place on May 10, 1922, to fill vacancies in the Bureau of Chemistry, for duty in the field, at $1200, with Congressional bonus for satisfactory service. The duties will include locating vessels bearing shipments of food and drugs, properly drawing samples from shipments, preparing reports and records, and examining and acting on customs invoices and manifests. Competitors will be rated on the following subjects: practical questions on methods of sampling—30 points; thesis, to be written in the examination room—20 points; education, training and experience—50 points.

Examinations have been announced for assistant examiner in the U. S. Patent Office, to be given May 10, 11, and 12, and on June 21, 22, and 23. Entrance salary is $1500 a year plus the bonus, with provision for promotion on merit to positions paying from $1650 to $3900. Competitions will be rated on the following subjects: methematics, 10; physics, 20; mechanical drawings, 20; language, 10; technics, 20; and optional subject, 20. The following optional subjects are offered: mechanical engineering, civil engineering, electrical engineering, general chemistry, electrochemistry, and chemical engineering.

The United States Civil Service Commission has announced examinations for junior technologist in the Bureau of Standards, at salaries of $1200 to $1500 a year. The examinations will be given May 24, July 5, and August 23. Examination will be given in the following optional subjects, and applicants must state in application all of these subjects in which they desire to be examined: rubber, leather, paper, textile, oil, and general technology. Competitors will be rated as follows: general chemistry and elementary physics, 20 points; mathematics up to and including calculus, 25 points; practical questions on each optional subject chosen (at least one optional must be taken), 30 points; education, training, and experience, 25 points.

Some Practical Aspects of Hydrogen Electrode Measurements[1]

By Paul E. Klopsteg[2]

Central Scientific Co., Chicago, Illinois

THE electrical (physical) measurements by which H-ion concentration can be determined, and the physicochemical theory upon which the measurements are based, are somewhat off the paths trodden by the average chemist, and for this reason he is likely to make only their casual acquaintance. It is not strange that this should be so; for there are so many new things purely chemical with which the average chemist must keep abreast that a subject which is only indirectly chemical must necessarily be put on the waiting list, where it usually remains. Besides, there have been so many hundreds of papers in the H-ion literature of the past half dozen years that the probability of any particular one of them having the sort of information he wants is small indeed.

If the writer has correctly interpreted the desires he has heard expressed, he would say that what the chemist wants to know about electrometric methods is what they can do for him in the solution of his own problems. Having the assurance that he can utilize the method, he wants to know how to proceed to get his results with least effort and outlay, yet with such ease, directness, and accuracy, that the net balance is a saving of time and money. This paper is an endeavor to answer these questions as accurately as possible; or, where a definite answer cannot be given, to point out the reason, and to suggest the best procedure for finding the answer.

Electrical methods of measurement and control in chemistry are possible because of the essentially electrical nature of the mechanism of a chemical reaction, *i. e.*, of the ions involved in the reaction. There are two distinctly different electrical properties of solutions that can be used to produce or control mechanical effects in a manner corresponding to chemical changes in the solution. These are, first, *conductance*, the property of a solution which permits an electric current to pass more or less freely. The second is the characteristic which results in a *potential difference* or electromotive force being set up between the solution and an appropriate electrode immersed in it. Both properties depend on the ion, or the atomic carrier of electricity, and no great strain on one's imagination is needed to see the reasonableness of the very close relation between the electrical properties and the chemical make-up of a solution.

Conductance (or more directly its reciprocal, *resistance*) of a solution is usually and most conveniently measured by means of a Wheatstone bridge of suitable type, employing alternating current to avoid polarization effects. However, the Wheatstone bridge is not the only device suitable for the purpose—several other methods well known in physics can, with suitable modifications, be used. It is beyond the limits of this discussion to go into details concerning conductance measurements. My object is to give a presentation of some of the practical aspects of the potential difference measurements, particularly applied to that potential difference which is a function of the concentration of the hydrogen ion. It should be said at this point that potential difference *cannot* be measured with a Wheatstone bridge, which is purely a resistance-measuring device.

When a compound is dissolved in water, some of its molecules are constantly splitting apart with electrical charges of opposite signs on the two parts. These oppositely charged ions are constantly seeking to recombine and many of them do recombine. When equilibrium is established, both the splitting-up process and the process of recombination take place at a constant rate, and the average number of free ions as compared with the total number of molecules gives us a measure of the so-called dissociation of the compound.

It is well known that the water molecule splits up into H and OH ions, but at equilibrium in pure water the total ionization is extremely small, the amount of H or OH ions at room temperature being only 1/10,000,000 gram-molecule per liter of water; the water is therefore 1/10,000,000 normal acid *or* alkaline. A neutral salt dissolved in water has no effect upon this equilibrium condition. Should an acid or base be put into the water, however, the former increases the number of H ions and the latter the number of OH ions, with the result that the rate of combination of oppositely charged ions becomes greater, and when equilibrium is established, the concentration[3] of H and OH ions, respectively, will be much greater than 1/10,000,000 normal.[4] With an acid like HCl, for example, it is easily possible to have such a high degree of ionization that in a molar solution of HCl, more than 80 per cent of the hydrogen is ionized. Such an acid, in which a relatively large proportion of the H atoms are ionized, is regarded as a strong acid. The strength of an acid is thus related to the number of H ions present in the solution. If, for example, a molar solution of acetic acid be made up, only 4.3 parts per thousand of the available hydrogen will be ionized. Bases behave similarly with respect to OH-ion concentration. These considerations bring out the distinction between *available* and *actual* hydrogen- or hydroxyl-ion concentration. In both HCl and CH_3COOH, the molar solution contains available hydrogen to the extent of 1.008 g. per liter; but in the first instance there is present in ionized form, ready to react, about 0.83 g., while in the second there are only 4.3 mg. Measurements of H-ion concentration involve a direct determination of the concentration of *actual* ionized hydrogen present. This cannot be found by titration with standard neutralizing solutions, which gives a measure merely of *total*, not *actual* reaction.

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[1] Presented before the Chicago Section of the American Chemical Society, October 21, 1921; before the South Bend and Mishawaka Section, November 22, 1921; and before the Indiana Section, December 9, 1921.

[2] Manager of Development and Manufacturing

[3] In this connection the writer takes the liberty of quoting from a statement he made several years ago in L. & N. Catalog No. 75, footnote, p. 6: "The discrepancies observed, especially in strong acids, between the ionic concentrations as measured by conductivity methods on the one hand and with the hydrogen electrode on the other, suggest that the quantity which we call H-ion concentration may not actually represent the degree of normality of hydrogen ions in the solution under test. Some have preferred to call this quantity 'activity.' Whatever name we choose to apply to it, the fact remains that in connection with a solution containing hydrogen ions there is a definite quantity susceptible to measurement, to the different values of which there correspond very definite characteristics of the solution. In this discussion we prefer to use the term 'hydrogen-ion concentration,' and in so doing we shall feel no concern regarding the objections which have been made to the use of the term."

[4] This fraction is more simply expressed as 1×10^{-7}, the negative exponent of 10 signifying that the power of 10 indicated is the denominator of the fraction. It is evident that any value between 1/10,000,000 and 1/1,000,000, the latter being the same as 10/10,000,000, can be expressed by a factor between 1 and 10, times 10^{-7}. The factor need not be purely integral, *i. e.*, it may be an integer plus a fraction, *e. g.*, 6.13×10^{-7}. The same statements hold for any decimal interval. This is the common method of expressing H-ion concentrations in terms of normal.

It is important to observe that, whatever the H-ion concentration may be when a substance is dissolved in water, the product of the concentration of H and OH ions is 10^{-14}. Hence, in designating acidity or alkalinity, it is merely necessary to mention the value of H-ion concentration, for its OH-ion concentration follows directly from this figure as shown a moment ago. Another point worth remembering is that, when the H-ion concentration is 10^{-14}, the OH-ion concentration is 10^0, or normal.

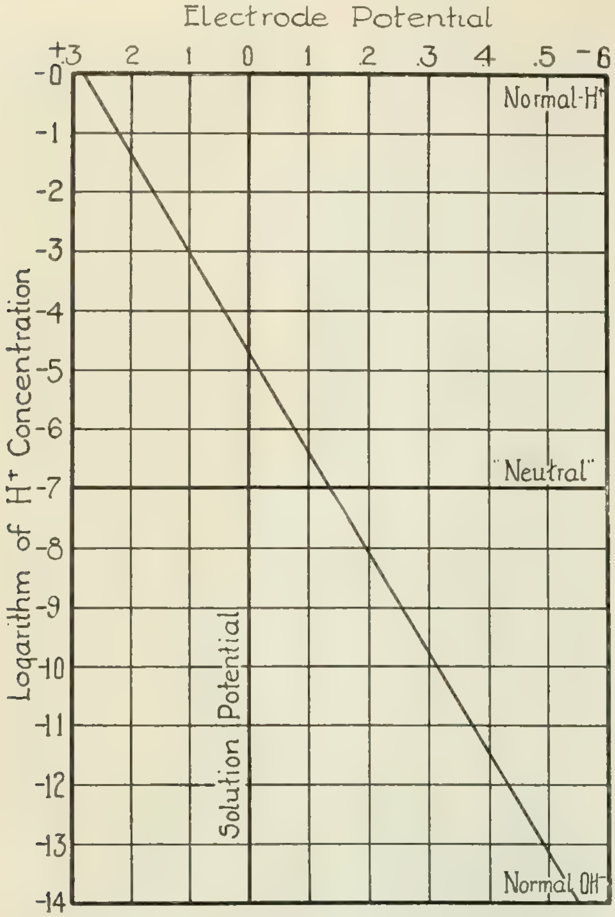

Fig. 1—Electrode potential of hydrogen electrode with reference to solution in which it is immersed, plotted against logarithm of hydrogen-ion concentration.

If we put an electrode of any metal or of hydrogen into a solution containing the corresponding ions, there will be set up, as a result of establishment of equilibrium between the solution pressure of the electrode substance and the osmotic pressure of the ions, a potential difference between the electrode and the solution. You will recall that potential difference (measured in volts or millivolts), sometimes called voltage, bears to electricity exactly the same relation that pressure bears to water. The higher the water pressure, the greater will be the speed with which a given quantity of water passes any point in a pipe or the greater the current. Similarly, the greater the potential difference, or electric pressure, the stronger the electric current resulting when a path is provided in which it may flow. But just as water pressure can exist statically, without causing a current of water, *e. g.*, when the pipe is stopped, so a potential difference can exist without causing a current, *e. g.*, when no circuit is provided. And it is this electrical pressure or voltage which varies as the concentration of the ions varies. It may be positive or negative with reference to the solution, *i. e.*, may have a deficiency or excess of electrons as compared with the solution, this depending on the solution pressure of the metal and the osmotic pressure or concentration of the ions of that metal.

The measured values of H-ion concentration, whether they be determined colorimetrically or by the methods which are here being discussed, derive their status from Nernst's equation,

$$E = E_0 + \frac{RT}{nF} \log_e C^+,$$

in which E is the potential difference between an electrode and the solution containing the corresponding ions; E_0 is the electrolytic potential, or the particular value of E when the ionic concentration C^+ in the solution is normal; R is the gas constant; T, the absolute temperature; n, the valence of the ion; F, the faraday, or 96,500 coulombs; and $\log_e C^+$ is the natural logarithm of the ionic concentration.

Taking the hydrogen electrode specifically, this is nothing more than a coating of platinum black deposited on an inactive metal, and exposed sufficiently long to a hydrogen atmosphere to become saturated. Such an electrode is positive to the solution when the concentration of hydrogen ions is normal; zero, when the concentration is somewhat less than 1/100,000; and is negative for lower values of concentration. This is shown in Fig. 1, which is a graph of Nernst's equation as applied to the hydrogen electrode. The values of potential used are based on observations, recorded in chemical literature, made with the dropping electrode or upon the curvature of the mercury surface in the tube of a capillary electrometer. They are approximately correct, probably within 10 millivolts. These potential values are plotted as abscissas, and the common logarithm of the concentration as ordinates. We have here adopted the convention of plotting the curve in the fourth quadrant, so that decreasing actual acidity is represented by a downward slope of the graph. This is also consistent with the fact that the logarithms are negative, since C^+ for hydrogen is always expressed as a fraction of normal, and the logarithm of a fraction is a negative number. On this scale of ordinates, -1 means 0.1 N; -2 means 0.01 N, etc., since $\log 1/10 = -1$ and $\log 1/100 = -2$. This scale, taken positively, is called the pH scale,[5] according to Sörenson's suggestion. Because of its convenience, biochemists have unanimously adopted the pH scale.

To convert a pH number[6] to actual H-ion concentration it is necessary only to find the number corresponding to the

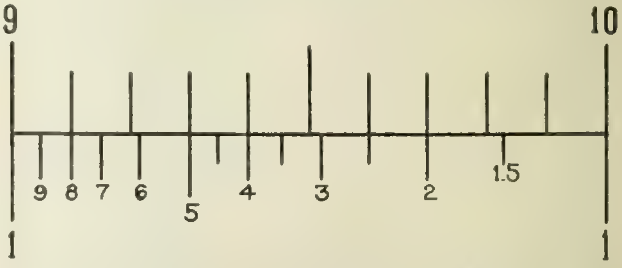

Fig. 2—Showing use of slide rule for converting pH into C^+ and vice versa. Upper scale represents scale of equal parts (whole length of rule) and lower scale the inverted logarithmic scale.

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[5] Properly written, this should be p_H, the derivation being that the number is proportional to the potential of the H electrode. For convenience in typographical work, pH is quite generally used.

[6] It is unfortunate that a single method for designating acidity and alkalinity has not been adopted. There are arguments for both the pH system and the numerical designation of H-ion concentration. The former, which is not as commonly used among chemists as the latter, has the advantage that pH values are linearly proportional to voltage, and the worker soon associates the pH value with perfectly definite characteristics of a solution. The latter, though it has definite physical meaning and is therefore more logical to use, is somewhat cumbersome, and greater effort is required to become fluent in its use.

pH value taken as a negative logarithm. As an illustration of this conversion process, suppose we wish to determine the H-ion concentration of a solution whose pH number is 9.54. The logarithm of the concentration sought is -9.54. The negative sign means that the corresponding value is a *fraction*, the denominator of which is the number whose logarithm is 9.54, or the fraction of normal concentration is 1/3,500,000,000. This mode of expression is awkward. A better way is to write it in accordance with the plan mentioned in Footnote 3, or $\frac{1}{0.35} \times 10^{-10}$, which is 2.88×10^{-10}.

Conversion from pH to C and vice versa is easily made with a slide rule having a scale of reciprocals, or with an ordinary slide rule, by inverting the slide. The scale of equal parts then reads the portion of the pH number after the decimal point, while the inverted scale reads the concentration factor which is multiplied by 10 with a negative exponent greater by 1 than the characteristic (preceding the decimal point) of the pH number. Fig. 2 will serve as a guide in following this example on a slide rule.

We now have the following picture: An electrode of platinum black, saturated with hydrogen, in a solution; a potential difference between the electrode and the solution, depending upon the H-ion concentration. The problem is to measure this potential difference and its variations as the concentration of H ions changes. To make the measurement with an electrical measuring instrument requires that means be found to connect the instrument to the electrode and solution, respectively, without introducing any additional potential differences into the circuit which, in the measurement, could not be differentiated from the potential difference we are trying to measure. We could make a metallic connection to the hydrogen electrodes, which would result in no difficulty; but how shall we connect to the solution and not run into trouble? Obviously we cannot use a metal electrode, dipping it into the solution, for this would be the seat of an unknown variable electromotive force. But a liquid junction can be established at which the e. m. f. is either negligible or very small and determinable; and if we can hold the second liquid invariable, and immerse in it a suitable electrode connected to our apparatus, the answer might be found. Although this would almost surely introduce an e. m. f. in series with the significant e. m. f., the former would be constant and determinable.

An obvious thought is to use as the second liquid, through which connection to the test solution is established, a solution of fixed H-ion concentration, in combination with a second hydrogen electrode. This gives us a connection such that the over-all potential difference will be measurable, and in which any variation of potential is due only to the changing H-ion concentration in the test solution. Fig. 3 illustrates the idea.

The same arrangement of electrodes, with the addition of a galvanometer and tapping keys with protective resistance, as shown in Fig. 4, serves a very useful purpose[7]—that of enabling the user to adjust the pH of a solution to be very closely the same as that of another reference or standard solution. Consider A and F immersed in solutions of different pH values, assuming B to be more acid than D. The electrical pressure (potential difference) is such that A tends to cause a flow into B; at the same time F tends to cause a flow of electricity into D, but the pressure is not so great, since D is less acid. If the circuit be closed through the galvanometer, a current flows, and causes a deflection, because of these unbalanced tendencies. Now let us imagine that B is a solution of exactly the proper acidity, and that we wish to render D as nearly like B as possible. All we need to do is to add H ions to D until the galvanometer shows no deflection when the key is closed. This method requires no knowledge of units—only of manipulation. An illustration would be to use a salt solution in B, and to titrate the corresponding acid with the corresponding base in D. Or, we might put a solution of known H-ion concentration in B, and use the arrangement in lieu of the more usual color indicator. This method has found much application in the adjustment of bacteriological culture media. Each end-point, of course, requires a particular solution of known pH value. By this and the other electrometric methods to be described, it is easily possible to titrate to within 0.01 pH unit. This is far closer than we can work with the best color indicators under the most favorable conditions.

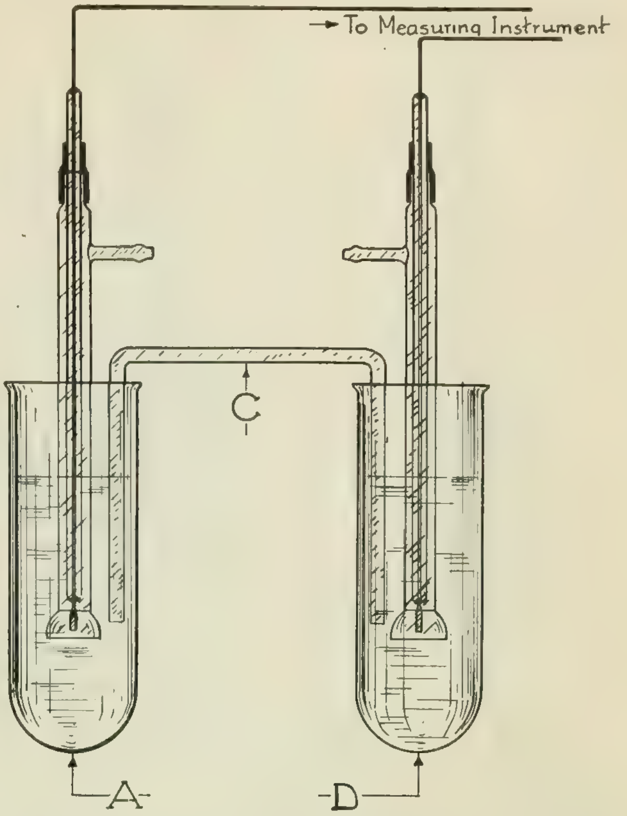

Fig. 3—A possible "gas-chain" arrangement, in which A is the standard solution, D the test solution and C the connecting tube. The latter is filled with a neutral conducting liquid, like KCl; the ends are plugged with cotton wool to prevent diffusion. The hydrogen electrode potential in A remains fixed, while that in D varies with the acidity of D.

The simplicity of application of color indicators makes them a very useful tool in the chemist's kit. As to the limits of their usefulness, we might say in general that turbidity or color in solutions, poor lighting conditions, and some kinds of salts and proteins make accurate determinations difficult, and when such conditions are encountered, the chemist should be on his guard lest he assume that he is getting greater accuracy than is actually the case. With a clear and colorless solution serving as the vehicle for a simple, well-defined reaction, we can expect an absolute accuracy of ±0.3 pH unit or slightly better. For many purposes this is ample, since, at the equivalent point of a titration, a few drops suffice to change the concentration of the H and OH ions by several pH units. The result is that in a simple titration with strongly ionized reagents almost any one of the usual indicators, such as methyl orange, phenolphthalein, azolitmin, and many others investigated by different workers, give a sufficiently accurate indication of the neutral point.

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[7] The arrangement and the application here described were suggested by the writer in *Science*, N. S., **52** (1920), 18, where a more complete description may be found.

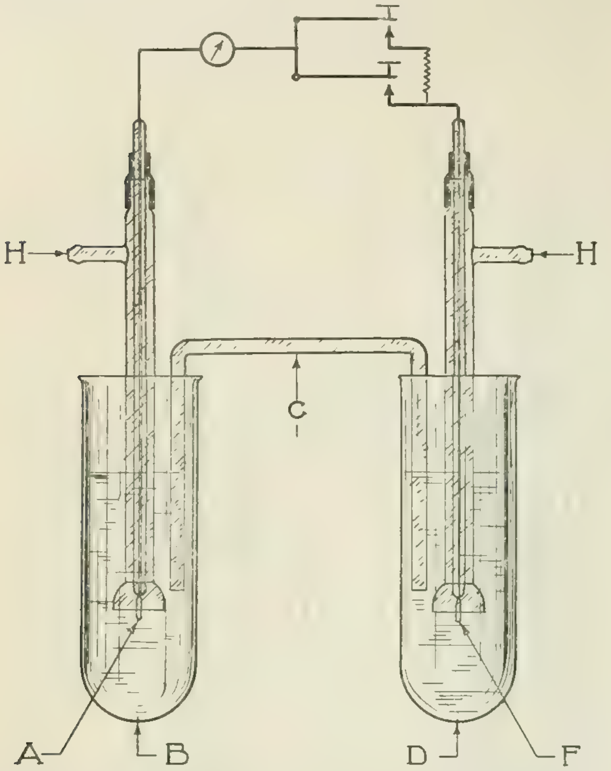

Fig. 4—Showing the application of the gas chain shown in Fig. 3 to simple titrations to a desired end-point. The hydrogen electrodes are connected through a galvanometer, to show equality of potential, and suitable tapping keys.

If, however, we desire to adjust an acidity or alkalinity in a particular region where there is no sudden change, it is necessary to be careful in the selection of the indicator, which should change color rapidly in the region in which we are interested. Methyl red, for example, could not be used as an indicator outside the limits 4.5 to 6. Another important point to observe is that all indicator ranges have been established with the hydrogen electrode, and that the color indicator is a secondary rather than a primary method in analysis or control. We may make the summary that the electrometric method is superior to the colorimetric method in the fact that with it we may often secure information that would be impossible to obtain by the indicator methods; and that in any case to which the hydrogen electrode can be applied, the results will be much more accurate than with an indicator. Where the color indicator methods can be used, they are to be recommended for their convenience.

Both the colorimetric and electrometric methods can to good advantage employ solutions of known pH, for check tests if for no other reason. Sörenson, Clark and Lubs, and others have worked out formulas for so-called "buffer mixtures" of any desired pH value. The "buffer mixture" is a mixture, such as an acetate, phthalate, or phosphate, which has great stability as regards changes in pH. For example, although very careful experiments show pure water to have an H-ion concentration of 10^{-7}, measurement on distilled water of high purity will seldom yield this value, because even the slightest acid or alkaline contamination (*e. g.*, carbon dioxide from the air) may change this exceedingly small concentration tenfold or a hundredfold. We can, however, produce a stable solution having a concentration of 10^{-7} by mixing 50 cc. of 0.2 *M* KH_2PO_4 with 31 cc. of the same strength NaOH, and diluting to 200 cc. Specific application of such a solution has already been indicated in the comparison method of titration, employing only a galvanometer.

Returning from this brief digression to the question of how to find quantitatively the variation in potential of the hydrogen electrode with reference to the test solution, we have seen that an electrode of fixed and determinable potential in an unvarying solution can be added to the chain, and that it affords a means for access to the quantity to be measured. Any such auxiliary electrode will do; but the type which has come into most general use, and which is generally accepted as the most satisfactory and convenient is the so-called calomel half-cell, or "calomel electrode." It has a variety of modifications in design and execution. Essentially it consists of pure mercury as the electrode proper, covered with a layer of pure calomel in solution of potassium chloride of known saturation, which itself has been saturated with calomel. The cell with 0.1 *N* KCl has probably been most closely studied; but there are certain advantages in the use of a more concentrated potassium chloride solution, which will be pointed out later. The cell has a side arm, or siphon tube, through which connection is established with the solution under test. Quite commonly, where accurate measurements are desired, a "connecting vessel" is used, containing saturated potassium chloride solution. This is interposed between the test solution and the calomel electrode for the purpose of eliminating liquid contact potentials. Since the latter seldom exceed a few millivolts, the connecting vessel can, in most practical work, be omitted. The common arrangement, known as a "gas chain," is shown in Fig. 5.

With an arrangement of this kind, we know that a certain potential difference exists between the mercury and the hydrogen electrodes, and that to any particular potential difference there corresponds one particular value of H-ion concentration. If we assume for the moment that this potential difference can be measured, we can apply our working formulas,

$$V = v - 0.0591 \log C^+,$$

or, since $pH = -\log C^+$,

$$V = v + 0.0591 \text{ pH},$$

to the determination of either C^+ or pH. The formulas come directly from Nernst's equation, which has previously been explained. In them V is the measured voltage, and *v* is the voltage which would be measured if the hydrogen electrode were in a solution having normal concentration of hydrogen ions; for in such a solution $C^+ = 1$, $\log 1 = 0$; hence $pH = 0$. Fig. 6 clearly illustrates the formulas. In this figure length

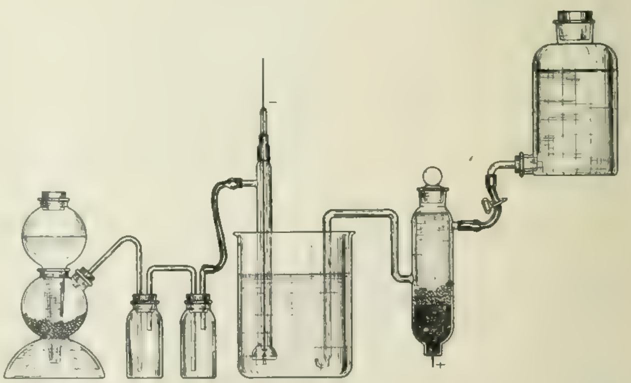

Fig. 5—Sketch of commonly used gas chain, showing hydrogen electrode supplied with hydrogen from Kipp generator, purified in wash bottles; calomel electrode with rubber tube connection to stock solution of KCl. Both electrodes in electrical contact with solution under test in beaker.

of line is proportional to voltage; AD represents the measured voltage, and AB the voltage which would exist between the calomel electrode and a hydrogen electrode in a solution of normal H-ion concentration. AO represents what is known as the electrode potential of the calomel electrode (0.560 volt at 18° C. for a 1.0 *N* KCl solution) although it is to be noted that this does not enter into our computations. The portion BD of the line corresponds to an abscissa in Fig. 1, O in the latter corresponding to the point O in Fig. 6.

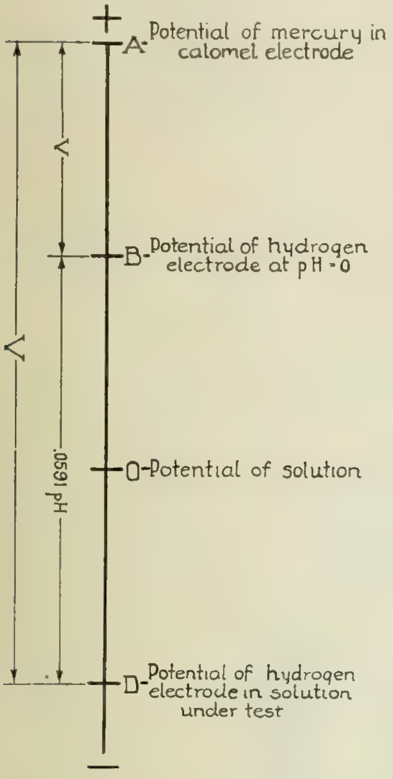
+
A
Potential of mercury in calomel electrode
V
B
Potential of hydrogen electrode at pH - 0
V
.0591 pH
O
Potential of solution
D
Potential of hydrogen electrode in solution under test
—

Fig. 6—Diagrammatic representation of relative potentials of calomel and hydrogen electrodes, and solution potential. This gives a graphic illustration of the working formula for the type of gas chain shown in Fig 5.

A very important practical question now is how to measure the voltage between the hydrogen electrode and the calomel cell. The hydrogen electrode is said to be in equilibrium when, on further exposure to hydrogen gas, its potential does not change in an unchanging solution. As has been stated, the calomel electrode has merely the unchanging reference potential, which may be likened to a fixed point with reference to sea level, from which we measure the electrical level of the hydrogen electrode. We find that to make this measurement accurately we must draw no current from the hydrogen electrode, for to do this would change its potential. We may compare it with a standpipe of small diameter, the level of the water in which changes if ever so little water be drawn off. Our problem in measurement of this voltage between hydrogen and calomel electrodes—in other words, of the gas chain—then resolves into this: It must be measured without permitting any appreciable flow of electricity through the electrodes.

In physics we have three methods, which have long been well known, for accomplishing this purpose. These are, first, the electrometer, of the quadrant type, which is relatively unimportant in this discussion; second, and also of small importance, the charging of a condenser by connection to the gas chain, and measuring the charge with a so-called ballistic galvanometer; the third and really important method is that employing a means for balancing a measurable, adjustable, potential difference against the unknown. To return to the analogy which has been used several times in this presentation, it may be likened to some such scheme of measuring the pressure of water in a standpipe by using a second standpipe in which the head, and hence the pressure, is adjustable and measurable, and "bucking" the second against the first. If, on opening the valve connecting the two pipes, there is no flow in either direction, as shown by a flowmeter, the two pressures are equal, and the first is known, since it is equal to the second which is measurable.

Potentiometer Methods

The plan of connections underlying all potentiometer or compensation methods is shown in Fig. 7. The similarity with this of the connections used in what is known as Hildebrand's method (Fig. 8) is apparent. The difference between the usual potentiometer method and this is that in the former a standard cell is used to establish a known fall of potential along the measuring circuit, while in the latter the fall of potential is ascertained at any one setting by reading a voltmeter. We observe that in each instance a source of current is needed to produce the necessary potential difference to balance that of the gas chain, and a galvanometer is required for indicating when that balance has been established.

Within the past few years a number of instruments have appeared on the market, or have been described in the journals, which employ the potentiometer principle. Among them may be mentioned the "ionometer," of Bartell, which followed McClendon's description of a direct reading potentiometer; another instrument called an "ion-o-meter," described by Elliott; the Bovie potentiometer; the pyrovolter, employing the balanced potential principle; the Wendt titration outfit, employing Hildebrand's connections; the Kelley electrometric titration apparatus, designed for determinations of chromium vanadium and manganese in alloy steels, and utilizing the change in potential during an oxidation-reduction process; the Roberts outfit, used in determining minute quantities of ferrous in the presence of ferric oxides; the Eppley titration apparatus; Hendrixon's improvised potentiometer, for iodometric titrations; the Type K potentiometer, the portable H-ion potentiometer, and the automatic recording potentiometer of Leeds & Northrup Co.; and a number of others. With a list as formidable as this before him, the poor chemist, lacking guidance, must be quite at sea in the matter of making the proper selection for his particular problem.

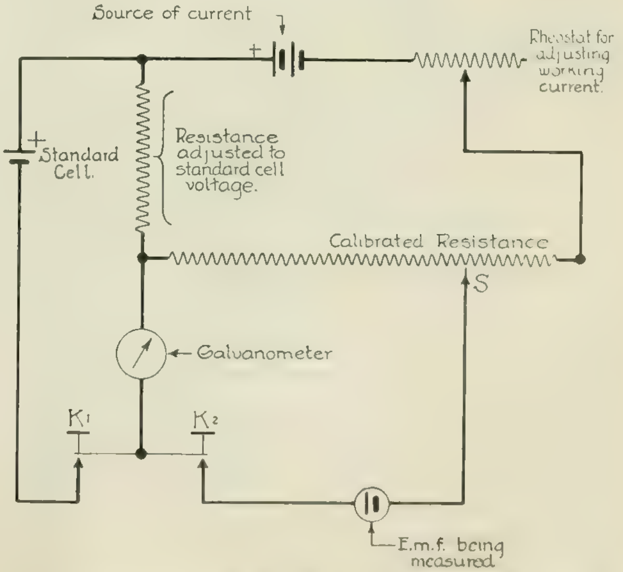

Fig. 7—Potentiometer circuits. To operate, K_1 is tapped and rheostat in upper circuit adjusted for zero deflection of galvanometer. This establishes a known current in the calibrated resistance For measuring unknown e. m. f., K_2 is tapped and S moved until galvanometer shows zero. The position of S is then read on a scale which is calibrated directly in volts.

SELECTION OF APPARATUS

It is impossible, of course, to discuss each of these instruments, and state where it is applicable. The writer can give only a few general suggestions which will be helpful in determining what outfit best suits certain requirements.

IS THE HYDROGEN ELECTRODE APPLICABLE?—In the first place, we must know whether or not the hydrogen electrode will be well behaved in the solution under test. There are many complex solutions, containing substances that are likely to "poison" the electrode and cause it to disregard with great obstinacy the expectation that it will observe Nernst's law. The best course is either to borrow an outfit from someone, or to let someone who has an outfit test the solution in which you are interested. Some work has been done on "poisoning" of electrodes, and the writer has been informed that a method has been devised for restoring "poisoned" electrodes, and removing from them the tendency to misbehave at any future time. Some of the "poisons" that have been mentioned are formaldehyde, sulfides, ammonia, and certain nitrates. There may be other substances in the solution upon which the platinum black in the electrode exerts a catalytic action. In solutions containing charged colloidal particles, it is impossible to measure the H-ion concentration because of the presence of these particles. According to Bovie, the silver remaining in a solution after precipitation with hydrochloric acid is sufficient in quantity to "poison" the electrode completely.

It is well to have at hand a buffer solution of known pH value which is altogether free from suspicion of poisoning the electrode. An electrode which in the test solution behaves peculiarly can then be quickly tested in the buffer solution, to determine whether or not it is poisoned. Should it, in this solution, give an indicated voltage far different from the value it should give for the known pH, a new electrode should be used. Several tests, on different electrodes, should be made before the hydrogen electrode is rejected as a possibility.

WHAT IS THE DESIRED ACCURACY OF MEASUREMENT?—Assuming that the hydrogen electrode will work, we should decide as to the accuracy with which the measurements are to be made. The impression prevails that instruments of highest accuracy and sensitivity are requisite to any kind of H-ion measurements. In ordinary works and laboratory processes high sensitivity is a hindrance rather than a help, because of the likelihood of the operator to draw erroneous conclusions from indications that are caused by insignificant factors. In general, solutions, and conditions of temperature and pressure, are not reproducible within very narrow limits, and other unknown and uncontrolled sources of small error are always likely to be present. For all practical purposes, an absolute accuracy of from 5 to 10 millivolts in the measuring instrument, and a sensitivity in the galvanometer of 2 to 5 millivolts *under conditions of test*, *i. e.*, in the gas-chain circuit, is ample. This accuracy corresponds to 0.1 pH unit, which is far closer than can be measured with a color indicator under the most favorable conditions.

For investigations involving the determination of another decimal place in a physicochemical constant, or the test of a theoretical equation, it is obvious that none but the highest grade potentiometer should be used, in conjunction with a highly sensitive galvanometer. It is obvious also that the use of such instruments imposes an obligation to exercise the greatest possible care in controlling all the conditions of the experiment. The conditions, and their control, lie outside the limitations upon this discussion.

Once the chemist has decided how accurately he wishes to measure, his choice of apparatus among the different available kinds will be largely influenced by his own ideas as to suitability of design and convenience of manipulation of the apparatus under consideration, and, to a minor degree, upon the persuasive power of the salesman offering it.

THE CALOMEL ELECTRODE

There is little choice among the various available designs. Each has some merits. Simplicity in this as well as in other parts of the apparatus is much to be desired. As regards the selection of degree of saturation of potassium chloride solution, concentrations greater than 0.1 *N* are to be recommended. Mudge and Fales have shown that the saturated potassium chloride electrode is extremely stable, that it minimizes resistance of the gas chain, and that slight changes in saturation have very little effect upon its potential. The same statement holds for the *N* KCl solution to a lesser degree. The latter has an advantage over the former in that no troublesome "creeping" of solution and crystallization of salt outside the vessel occurs, although in the former case the trouble from creeping can be obviated by setting limits to it with vaseline or paraffin.

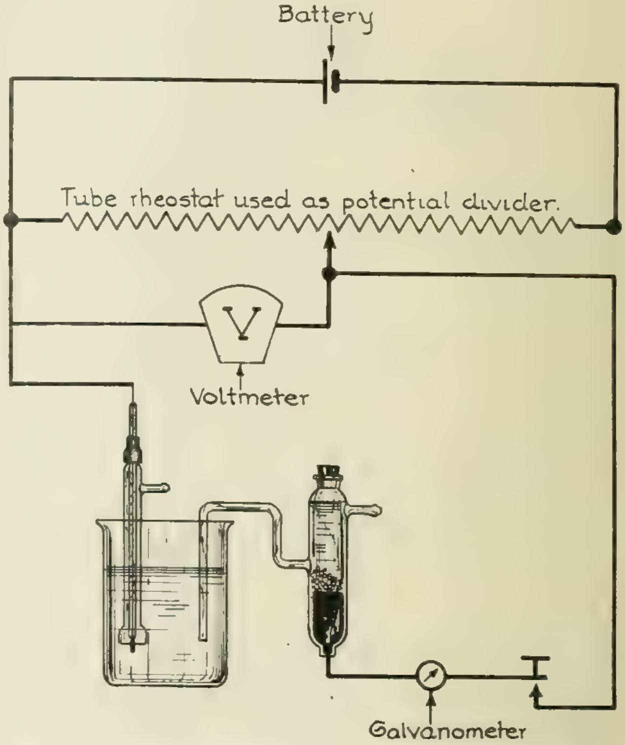

FIG. 8 —Hildebrand's connections for measuring gas-chain voltage. The e. m. f. from the gas chain is balanced by adjustment of the potential divider until galvanometer shows zero. The voltmeter, permanently connected as shown, then reads the potential difference which was required to balance the unknown e. m. f.

The reservoir vessel should contain potassium chloride of the same concentration as that in the cell, saturated with calomel. The cell should be flushed out from time to time by allowing some of the stock solution to run through the siphon arm. This prevents contamination of the cell from the testing solution. In flushing, care should be taken to displace all air bubbles in the siphon tube, since these introduce a high resistance into the galvanometer circuit and render the indications sluggish and insensitive.

In work of the degree of accuracy we are considering, the connecting vessel may be omitted for reasons already stated. Errors due to liquid junction potentials are least when a calomel electrode with saturated potassium chloride is used.

THE HYDROGEN ELECTRODE

Successful deposition of platinum black on the electrode is a fairly simple matter, for which there are many methods. A procedure which the writer has found invariably successful is to use a weak solution of platinic chloride—about 2 per cent—and, after having most thoroughly cleaned the platinum, introduce the electrode and a piece of clean platinum wire, or another electrode, into the solution. These two electrodes are connected to two dry cells in series. As soon as there is a copious evolution of gas, reverse the connections, and continue reversing at the same indication, for several minutes. The intervals between reversals will be 10 to 15 seconds.

Some workers prefer to use gold as the base upon which to deposit the platinum black, while others have gold-plated their platinum base. Presumably this shortens the time for the electrode to reach equilibrium because of the smaller absorption of hydrogen by gold than by platinum.

The basis for choice of any one of the many forms of hydrogen electrode described in the literature cannot be gone into here. In general, the bubbling type (Hildebrand, Bovie, Wendt) is satisfactory for a great variety of measurements.[8]

SOURCE OF HYDROGEN

The most convenient source of hydrogen is the steel drum containing the compressed gas, readily obtainable in most cities. Electrolytic hydrogen is desirable. The drum should have a reducing valve for regulation of gas pressure, and the gas is led to the apparatus preferably through copper tubing or undercured gum tubing, to reduce loss of gas by diffusion. Electrolytic generators on a laboratory scale have been used with success, employing sodium hydroxide with nickel or iron electrodes. The Kipp generator is also a suitable source. In any case, the gas should be passed through wash bottles containing solutions for removal of such impurities as oxygen, arsine (from impure zinc in Kipp generator), acids, and possible traces of foreign gases which might previously have been in the hydrogen cylinder. A common practice is to pass the gas first through alkaline permanganate, then pyrogallol, and finally pure water. When small quantities of solutions are being titrated or tested, *e. g.*, in a culture tube or other small vessel, the gas itself serves admirably as an agitator. In larger vessels, a mechanical stirring device is necessary for intimate mixing during a titration.

TEST OF APPARATUS

One test has already been mentioned, to determine the condition of the hydrogen electrode. The same kind of test is excellent as an over-all check of the apparatus. This consists of using a standardized buffer solution of any convenient pH value in place of the test solution, and measuring the voltage. If this is only several (10 to 20) millivolts different from the calculated value for that particular pH, it is probable that the difference is a departure in the calomel electrode from the assigned value for the concentration of potassium chloride being used, and to other sources of minor e. m. f.'s. Adjustment can then be made in the calculations. A check on this test is to use another solution of different pH and to note whether the same difference in millivolts is observed.

It is to be noted that with a preliminary test of this sort it is unnecessary to devote much painstaking work to making up the calomel electrode. The only requirement is that its electrode potential be unvarying, and this condition becomes established within several days after preparation of the cell.

MEASUREMENT OF pH—When it is desired to know the actual H-ion concentration or pH of a given solution, a direct measurement of voltage of the gas chain is sufficient, from which the desired value is calculated.

CONVERSION OF MEASURED VOLTAGE INTO pH

This is accomplished by using the formula previously given: $\mathrm{pH} = \frac{V - v}{0.0591}$. V is the observed voltage, and *v* the calomel cell potential referred to the hydrogen electrode at $\mathrm{pH} = 0$; the factor 0.0591 is the number of volts corresponding to one pH interval at 25° C. There is a small temperature correction which in routine work at "room" temperature may be disregarded. The otherwise necessary computations are eliminated by the use of tables.[9] A still simpler and more convenient way is to use a specially designed slide rule of straight or circular pattern, as recently described by the writer.[10] An ordinary slide rule is also a great convenience, although in this case a mental subtraction $(V - v)$ must first be made.

ELECTROMETRIC TITRATION

This application of the hydrogen electrode with its measuring and indicating instruments is one of the most important, from the chemist's standpoint. Titration with a standardized acid or basic solution to some particular end-point (equivalent point), and adjustment of a medium to a particular pH value for optimum experimental conditions, are illustrations.

The usual titration curves, of the type obtained by Hildebrand,[11] are obtained by plotting voltage or pH against volume of solution added. Near an equivalent point there is a sudden and usually large change in voltage. This change, shown by a sudden large galvanometer deflection, may be taken as an indication of the equivalent point, or where higher accuracy is needed, a curve may be plotted and the equivalent volume more closely estimated. An accuracy of one or two parts per thousand is easily obtained. When the pH of an equivalent point is known, or when it is desired to adjust a solution to a definite pH value, the voltage may be set for the proper value, and titration continued until the galvanometer shows a balance. In all such measurements a light tap on the galvanometer key should be employed until a balance has been nearly obtained, after which the circuit may be kept closed. This precaution avoids upsetting equilibrium conditions in the gas chain.

In a limited time it is impossible to do justice to an enumeration, even with the briefest descriptions, of the many successful applications that have been made of the hydrogen electrode. For these reference must be made to the literature. In Clark's excellent book "The Determination of Hydrogen Ions" there is given a bibliography, classified according to applications, which gives one an excellent idea of what has been done up to 1920. Since that time other applications have been made, and more are added with each new issue of the chemical journals.

One application has been suggested by several chemists interested in teaching, the value of which is borne out in the experience of those who have made electrometric titrations with the hydrogen electrode. It deserves special emphasis. There is probably no method or apparatus that can be put in the hands of a student which is so illuminating and which so readily explains the meaning of such terms as "acidity," "actual reaction," "total reaction," "alkalinity," "hydrolysis," and others, as a simple apparatus for measuring hydrogen electrode potentials. With a clear understanding of these matters he has a "stock in trade" which will save him much perplexity and which will aid him in clear insight into many of the problems which he must tackle when he begins the practice of his profession.

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[8] Other practical points in connection with the use of the hydrogen electrode are mentioned in Leach's "Food Inspection and Analysis," 4th edition, 1027.

[9] For example, Schmidt and Hoagland, *Univ. Calif. Pub. Physiol.*, **8** (1919), 23.

[10] *Science*, **54** (1921), 153.

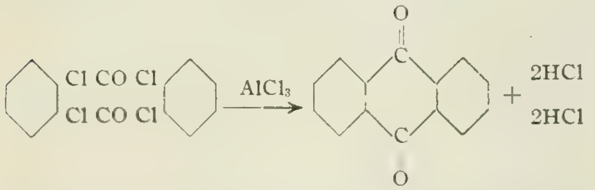
[11] *J. Am. Chem. Soc.*, **35** (1913) 847.

The Reactions of Phosgene with Benzene and *m*-Xylene in the Presence of Aluminium Chloride[1,2]

By Robert E. Wilson[3] and Everett W. Fuller

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts

On account of the great reduction in the cost of producing phosgene, which was brought about by war-time developments, this Laboratory has undertaken a study of possible new methods of utilizing this reactive compound in certain syntheses which now appear to be within the range of commercial possibility. The initial aim of the work described in this article was to produce anthraquinone from phosgene and benzene by the Friedel and Crafts reaction:



Although anthraquinone was not secured, the results obtained are of interest, as they represent a much more thorough study of the reactions between phosgene and benzene (and its homologs) than has been published previously.

The reaction between phosgene and benzene in the presence of anhydrous $AlCl_3$ gives benzoyl chloride and benzophenone but no trace of anthraquinone.

The reaction takes place in two stages, with the intermediate formation of the compound $C_6H_5COCl:AlCl_3$ which can be hydrolyzed to give benzoic acid. This reacts very rapidly with more benzene, however, and the final product is almost entirely benzophenone irrespective of changes in temperature, method of mixing, ratio of reacting substances, etc.

When CS_2 is used as a diluent a large part of the product can be obtained as benzoic acid. Evidence is presented to show that this is due to the slight solubility of the intermediate benzoyl chloride-$AlCl_3$ compound in CS_2 which is thus removed before it has opportunity to react with more benzene.

m-Xylene gives with phosgene a di-xylyl ketone with at least two of the methyl groups ortho to the carbonyl group.

Attempts to change this di-xylyl ketone to a derivative of anthraquinone by oxidation were not successful.

In one of their early papers, Friedel and Crafts[4] mention that by adding anhydrous aluminium chloride to a mixture of benzene and phosgene, they secured benzophenone and a small amount of benzoic acid. No trace of anthraquinone was found. Later experimenters[5] used xylene in place of benzene and obtained the corresponding phenones and acids, but no evidence of a quinone linkage was reported. No further work on the reactions of phosgene with benzene, toluene, or xylene is reported in the literature to the knowledge of the authors.

Attempts to Make Anthraquinone

By varying the experimental conditions the attempt was made to carry the reaction beyond the stage of the formation of benzophenone and thus secure anthraquinone. However, by none of the methods tried was it found possible to cause more than one phosgene molecule to react with a single benzene molecule even when a large excess of phosgene was used. For additional proof, benzophenone was treated with phosgene and aluminium chloride at different temperatures. There was no evidence of any reaction taking place and the benzophenone was recovered unchanged. Also, benzoyl chloride was treated with an equivalent amount of aluminium chloride in the hope that two molecules might mutually react with each other and thus give anthraquinone. But no reaction was noted up to near the boiling point of the benzoyl chloride, when charring and decomposition of the latter took place. No definite new compound could be isolated.

These results are in accord with the customary observation that it is very difficult to make two negative groups enter an aromatic ring ortho to each other. They also agree with the results of V. Meyer[6] who found it impossible to put two acetyl groups on benzene by the Friedel and Crafts reaction.

By reducing the benzophenone to diphenylmethane it was, however, found possible to make it react with more phosgene, but the resulting product was tarry, and was not identified. This indicates again that the negativity of the keto group is what prevented further reaction with the phosgene.

Reactions between Phosgene and Benzene

Although there seemed to be little likelihood of being able to prepare anthraquinone by this method, a study was made of the principle factors influencing the reaction between phosgene and benzene to form benzoyl chloride and benzophenone.

The mechanism of the action of aluminium chloride in the Friedel and Crafts reactions has been studied by a number of investigators.[7] For reactions of the above type, the chloride appears to form a compound with one or both of the reacting substances and thus to render them active. In the case of phosgene, three fairly stable molecular compounds with aluminium chloride are claimed to have been isolated,[8] while with benzoyl chloride and benzophenone molecular compounds, containing mole for mole, have been found. The aluminium chloride thus bound up renders its own molecule active but is not available for activating other molecules.

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[1] Presented in preliminary form before the Division of Organic Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] Published as Contribution No. 42 from the Research Laboratory of Applied Chemistry, M. I. T.

[3] Director, Research Laboratory of Applied Chemistry, M. I. T.

[4] Friedel, Crafts and Ador, *Ber.*, **10** (1877), 1854.

[5] Ador and Pelliet, *Ibid.*, **11** (1878), 399.

[6] *Ber.*, **29** (1896), 1413.

[7] Boeseken, *Rec. trav. chem.*, **19** (1900), 19; **20** (1901), 102; **24** (1905), 6; Perrier, *Ber.*, **33** (1900), 815; Krarberg, *J. prakt. chem.*, **61** (1900), 494.

[8] Band, *Compt. rend.*, **140** (1905), 1688.

TABLE I—REACTIONS BETWEEN BENZENE AND PHOSGENE
(All quantities are given in relative moles)

No.	Benzene	Phosgene	$AlCl_3$	CS_2	Benzoic Acid	Benzophenone	Benzoic Acid Benzophenone	METHOD
1	4	Excess	1	..	0.01	0.89	..	Phosgene into benzene and $AlCl_3$ at 4° C.
2	4	Excess	1	..	0.01	0.87	..	Phosgene into benzene and $AlCl_3$ at 80° C.
3	4	2	1	..	0.01	0.55	..	Benzene to mixture of phosgene and $AlCl_3$
4	2	1	1	..	0.01	0.55	..	$AlCl_3$ to mixture of benzene and phosgene
5	2.5	1	1	..	0.01	0.63	..	$AlCl_3$ to mixture of benzene and phosgene
6	2	1	1	..	0.01	0.70	..	Same as 4 and kept under 1 atmos. gage pressure
7	2.5	1	1	..	0.01	0.75	..	Same as 4 and kept under 1 atmos. gage pressure
8	2	1	0.23	..	0.01	0.18	..	$AlCl_3$ to mixture of benzene and phosgene
9	2	1	0.35	..	0.01	0.27	..	$AlCl_3$ to mixture of benzene and phosgene
10	1	1	1	..	0.01	0.48	0.021	$AlCl_3$ to mixture of benzene and phosgene
11	1	1	1	0.10	0.05	0.43	0.116	$AlCl_3$ to mixture of benzene and phosgene
12	1	1	1	0.50	0.10	0.41	0.244	$AlCl_3$ to mixture of benzene and phosgene
13	1	1	1	1	0.25	0.33	0.760	$AlCl_3$ to mixture of benzene and phosgene
14	1	1	1	2	0.36	0.29	1.24	$AlCl_3$ to mixture of benzene and phosgene
15	1	1	1	2.5	0.33	0.23	1.43	$AlCl_3$ to mixture of benzene and phosgene
16	1	1	1	4	0.38	0.25	1.52	$AlCl_3$ to mixture of benzene and phosgene
17	1	1	1	4	0.59	0.17	3.47	Benzene added drop by drop to others—kept cold
18	1	1.5	1	4	0.01	0.39	..	$AlCl_3$ added very slowly to others
19	1	Excess	1	4	0.01	0.25	..	Phosgene added very slowly to others
20	2	1	1	4	0.03	0.52	..	$AlCl_3$ to mixture of benzene and phosgene
21	..	..	..	..	0.01	0.24	..	Al amalgam in benzene + HCl and then + phosgene
22	..	..	..	..	0.01	0.16	..	Al + $HgCl_2$ in benzene + phosgene
23	..	..	..	..	0.01	0.08	..	Al in benzene + HCl + phosgene
24	..	..	..	..	No action		..	Anhydrous $FeCl_3$(1 mole)

EXPERIMENTAL STUDY OF BENZENE-PHOSGENE REACTIONS

EXPERIMENTAL METHOD—In studying the effect of changing various conditions, the general method of procedure was as follows, unless otherwise specified. A weighed amount of phosgene was absorbed in a known amount of benzene cooled with ice and salt. The aluminium chloride was then added slowly and the flask was allowed to stand in the ice bath for several hours until the reaction had proceeded to a considerable extent and then was left at room temperature for 12 to 15 hrs. The mixture was then added to ice water, which decomposed the aluminium chloride compounds with the separation of an oil consisting of benzophenone, benzoyl chloride, and any excess benzene that might be present. The oil was treated with caustic soda solution to hydrolyze the benzoyl chloride and remove it as sodium benzoate. On acidification of the extract benzoic acid was precipitated and recovered. In the following work the benzoyl chloride is reported as benzoic acid. The remainder of the oil was dried and fractionally distilled to give benzene and benzophenone.

EFFECT OF DIFFERENT VARIABLES—The effect of various conditions of the yields and on the course of the reactions may be determined from a study of the data given in Fig. 1 and in Table I. In considering the yields relative values should be given greater weight, as small differences in actual yields were unavoidable even under the same experimental conditions. All yields were based upon the purified product.

Time—Fig. 1 indicates the results that were secured by removing 100-cc. samples at various times from a mixture of relative moles of phosgene and aluminium chloride in an excess of benzene that was maintained at 4° C., and analyzing for benzoyl chloride and benzophenone. The formation of excess benzoyl chloride, over that reacting with more benzene to give benzophenone, starts in slowly, gradually increases, and reaches a maximum in 5 to 6 hrs., after which it falls off again. Benzophenone also starts in very slowly but constantly increases to a maximum at somewhat less than 24 hrs. The reaction is evidently completed within 24 hrs., at 4° C.

A two-stage reaction with the intermediate formation of benzoyl chloride is clearly indicated. Thus it will be noted that at the very start of the reaction more benzoyl chloride than benzophenone is found. As time goes on the reaction as a whole accelerates, as measured by the total conversion of benzene to one of the two forms; but the quantity of intermediate product increases comparatively slowly while the end-product increases rapidly. The maximum rate of forming benzophenone coincides with the maximum momentary concentration of benzoyl chloride, as would be expected. Thereafter, as the rate of forming benzoyl chloride drops off, as a result of exhaustion of the *phosgene*, the small excess which had been built up quickly disappears, and eventually benzophenone is substantially the only product obtained.

It is not possible to make an exact comparison because of certain uncertain variables having to do with the formation of the aluminium chloride compounds, but it would appear from these data that the *specific* reaction rate between benzoyl chloride and benzene is about ten times as great as that between phosgene and benzene under conditions similar to those prevailing above. It is accordingly impossible, under such conditions, to carry the reaction on anywhere nearly to completion without having the end-product present in much larger amounts than the intermediate product (eventually benzoic acid).

Since the latter material is the only one with a large market at the present time, much of the following work had as its immediate aim the altering of the conditions of the reaction so as to favor the formation of benzoic acid rather than benzophenone, either by speeding up the first reaction or slowing down the second. The yields of the product per mole of the more expensive raw materials (aluminium chloride and phosgene) were also of importance.

Temperature—Expts. 1 and 2 in Table I were run in an identical way except for the temperature difference. The yields and products were the same.

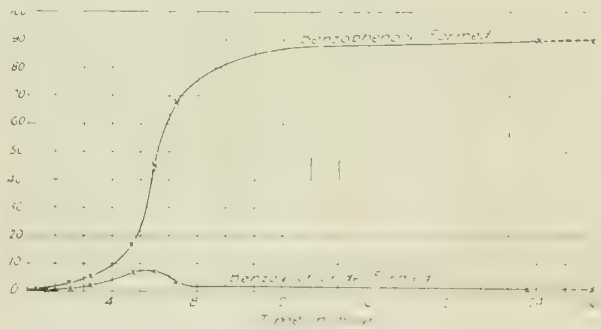

FIG. 1

Method of Mixing—As shown in Table I, Expts. 1, 2, 3, 4, etc., the methods of mixing the constituents were varied in all possible ways. The products were always the same, however, and the yields were not affected where the same proportions of constituents were used.

Pressure—The result of using pressure is indicated in Expts. 6 and 7. Pressure probably acts simply as a means of hindering escape of phosgene and thus gives a somewhat higher yield.

Proportion of Constituents—The molecular proportions of constituents are given by the equations for the reaction and must be used to secure anything approaching 100 per cent yields. On account of the volatility of phosgene an excess of it or of benzene helps the yields per mole of the other constituent by maintaining sufficient gas throughout the run to give the theoretical yields. The effect of increasing amounts of aluminium chloride is shown in Expts. 8, 9, and 4. One mole of aluminium chloride is evidently united with and removed from its active state by each mole of product formed and so a theoretical amount of aluminium chloride must be used. As stated before, these molecular compounds of aluminium chloride have been isolated, but in further confirmation of their formation in these reactions a crystal obtained in one of the experiments was analyzed and found to correspond to the formula $C_6H_5COC_6H_5.AlCl_3$.

Substitutes for $AlCl_3$—Several substitutes for aluminium chloride were tried, as is indicated in Expts. 21, 22, 23, and 24, but none of these proved satisfactory. Anhydrous ferric chloride can be used in place of aluminium chloride in many of the Friedel and Crafts reactions, but with phosgene and benzene it appeared to be inert.

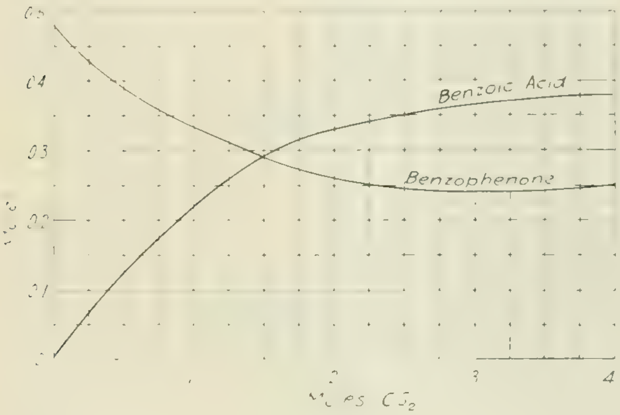

FIG. 2

Use of CS_2 as a Diluent—The result of using carbon disulfide as a diluent may be seen by comparing the experiments in which no disulfide was used with those in which varying amounts were used, Expts. 10 to 16. The comparison is brought out clearly in Fig. 2. A marked increase in the amount of benzene (proportion of benzene) remaining as benzoic acid (benzoyl chloride) is shown up to a carbon disulfide concentration of 2 moles to 1 of benzene, while beyond this point addition of carbon disulfide does not greatly affect the results. A corresponding decrease in benzophenone is found to the same concentration of carbon disulfide.

This marked increase in the relative amount of benzoic acid to benzophenone with increasing carbon disulfide was further investigated. As stated before, the benzoyl chloride that is formed as an intermediate product in the preparation of benzophenone forms a definite molecular compound with aluminium chloride. It was suggested by Prof. J. F. Norris that this intermediate molecular compound might be rendered less soluble in the reacting medium by the presence of CS_2. It would thus be removed from the sphere of activity with a resulting increase in the relative amount of benzoic acid obtained in hydrolysis.

Solubility data obtained in this Laboratory[9] indicate this explanation to be correct. The benzoyl chloride-aluminium chloride compound was isolated as a yellow solid and its solubility determined for varying mixtures of carbon disulfide and benzene. The results follow:

	Temperature 4° C.	Solubility
Per cent CS_2	Per cent Benzene	G. per 100 Cc.
100	0	1.4
75	25	2.6
50	50	7.7

Furthermore it was noticed that in runs where carbon disulfide was used and the yields of benzoic acid were high a heavy dark oil separated out in the bottom of the flask. Although this substance was a liquid where a solid would be expected, it undoubtedly contained the benzoyl chloride-aluminium chloride compound which was thus separated to some extent from the incoming benzene. The composition of the dark oil was not constant, but an analysis of that obtained at the end of one of the runs gave 9 per cent of benzoic acid, 53 per cent aluminium chloride, 17 per cent of benzophenone, and 21 per cent of phosgene, with possibly a little benzene.

Further to prove this point, Expt. 17 was made, in which benzene was dropped very slowly into a cold mixture of carbon disulfide, phosgene, and aluminium chloride. This gave the best possible conditions for precipitating the intermediate molecular compound out of solution as it is formed and before it could come in contact with more benzene. As was expected, the yield of benzoic acid was very large and that of benzophenone was low, and some procedure similar to this is probably the best way to obtain a high yield of benzoic acid. On the other hand, when either aluminium chloride or phosgene was added very slowly to a mixture of the other three, it gave a chance for each new mole of benzoyl chloride to react with more benzene; thus the principal product was benzophenone, as shown in Expts. 22 and 23.

The above experiments with carbon disulfide were all made with just one mole of benzene for each mole of aluminium chloride and phosgene and the discussion holds only for such a case. If, however, more than a mole of benzene is used per mole of aluminium chloride, the product will eventually be all benzophenone, since the intermediate compound will slowly redissolve and react with the excess benzene if sufficient time is allowed. Expt. 20 indicates this. Where no carbon disulfide is used, on the other hand, the much greater solubility of the benzoyl chloride-aluminium chloride compound in benzene brings about complete reaction to benzophenone, regardless of the ratio between benzene and aluminium chloride used (Expts. 1 to 10).

COMMERCIAL POSSIBILITIES[10]—While the foregoing investigation has not been directed primarily to the commercial aspects of the process, it seems worth while to consider briefly this phase of the problem.

Although the listed price of benzophenone is quite high, it has little use except for scientific purposes and the demand is not large enough to warrant a commercial installation. If its availability at much lower prices should ever develop a demand for this product, the above-described method is certainly admirably adapted for commercial production, as the yields are high (85 to 90 per cent), the product clean, and the raw material cost quite low, a very small fraction of the present quotations for pure benzophenone.

For benzoic acid, on the other hand, there is a very ready market, and material such as that prepared by the above reaction, which is entirely free from chlorine in the ring (as distinguished from the product made by chlorinating toluene, which gives trouble in this respect), has a large and active market. It is for this reason that the effort was made in the foregoing study to increase the yield of benzoic acid as compared with benzophenone, and this was found possible by slowly adding benzene to the other components dissolved in carbon disulfide. The cost of this process on a commercial scale depends partly on the losses of carbon disulfide and on whether the process can be made continuous by drawing off the lower layer of oil and adding the other constituents to the carbon disulfide. The small amount of benzophenone found as a by-product could be readily converted to benzoic acid by fusing it with caustic soda (recovering the benzene evolved), dissolving in water, and acidifying with sulfuric acid. This process gives 90 per cent yields without difficulty.

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[9] D. I. Gross, undergraduate thesis, M. I. T.

[10] The recommended process has been covered by U. S. Patent Application.

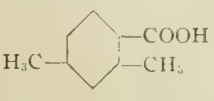
Another possible process would be to carry the reaction through to benzophenone without the use of any carbon disulfide, and then to form benzoic acid by the above-mentioned fusion process applied to the entire product. The high chemical cost of this process would be largely or entirely counterbalanced by the more rapid reaction rate and the absence of the fire risk and losses attendant upon the use of large amounts of carbon disulfide.

Rough estimates of the total costs of these two processes indicate that it should be possible to produce chlorine-free benzoic acid for about the present quotations (60 cents per lb.) for the present U. S. P. material, not allowing for sales cost or profits. If there should be enough demand for benzophenone to consume the small amount produced as a by-product in the carbon-disulfide process, or if the price of chlorine-free benzoic acid should be stabilized around 80 cents per lb., the process would appear to have distinct commercial possibilities.

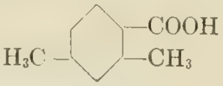
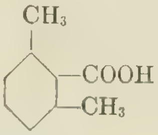
Reaction between Phosgene and Meta-Xylene

A brief study was made of the product formed by the reaction of phosgene and xylene in the presence of aluminium chloride. Phenyl-*o*-tolyl ketone is known to give anthraquinone on heating with lead oxide or with manganese dioxide and sulfuric acid.[11] It has also been shown that phosgene and xylene react to give a ketone with at least two of the methyl groups ortho to the carbonyl group.[12] The attempt, therefore, was made to bridge across these ortho methyl groups of di-*m*-xylyl ketone by oxidation and thus to secure a substituted anthraquinone.

PREPARATION OF DI-*m*-XYLYL KETONE—*m*-Xylene was prepared by the boiling of a commercial xylene (b. p. 138°-142°) with dilute nitric acid (1:3) for several days to oxidize the *o*- and *p*-xylenes, and then washing with caustic soda solutions, steam distilling, and carefully fractionating with a column containing glass beads. A xylene was thus secured boiling at 139.0° to 139.4°, where *m*-xylene boils at 139.2°. This xylene was treated with phosgene and aluminium chloride and the resulting product was worked up in the usual way. The dixylyl ketone was secured in the form of an oil boiling at 345° to 348°. The reaction was similar to that for the formation of benzophenone, except that when carbon disulfide was used as a diluent the *m*-xylene gave only a very small amount of an acid derivative even when the reaction was carried out under the conditions that had proved most favorable for the formation of benzoic acid. The acid formed in the case of *m*-xylene was entirely



melting at 126°.

CONSTITUTION OF DI-*m*-XYLYL KETONE—Since it was necessary to have one or more of the methyl groups in the dixylyl ketone ortho to the carbonyl group in order to be able to oxidize the ketone to an anthraquinone derivative, the positions of these methyl groups were first checked up.[13] The ketone was fused with caustic soda and the acids secured from the resulting sodium salts were determined. The major portion consisted of the  acid melting at 126° and which gave an amide melting at 179°. About 10 per cent was the  acid melting at 97° to 99°. Each of these acids indicates a carbonyl group in the ketone with at least two methyl groups ortho to it.

OXIDATION OF DI-*m*-XYLYL KETONES—Attempts to oxidize the dixylyl ketone were made at various temperatures. Lead oxide, manganese dioxide and sulfuric acid, potassium dichromate in acid and alkaline solutions, potassium permanganate in acid and alkaline solutions, and fusion with sodium peroxide had no effect upon the ketone. Potassium dichromate in concentrated sulfuric acid and chromic oxide in acetic acid decomposed the ketone while nitric acid in sulfuric acid formed nitro derivatives. Refluxing with 1:1 nitric acid gave a semisolid mass from which a calcium salt of an acid was separated. This yielded 9.4 per cent CaO on ignition, which corresponds to one mole of calcium to two moles of dixylyl ketone acid (9.7 per cent CaO). The oxidation, therefore, resulted merely in attacking one of the methyl groups in each molecule. No further attempts at oxidation were made.[14]

Acknowledgment

The writers desire to express their appreciation of the many helpful suggestions of Dr. C. S. Venable and Dr. J. F. Norris.

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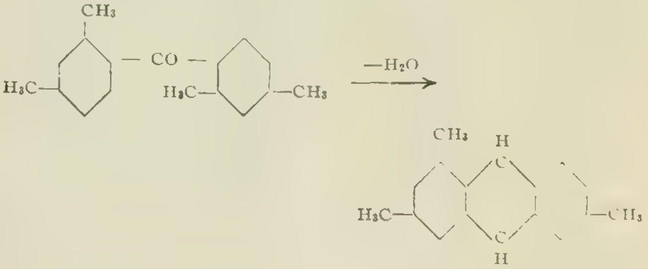
[11] Behr and van Dorp, *Ber.*, **6** (1873), 754; **7** (1874), 16.

[12] Ador and Meier, *Ibid.*, **12** (1879), 1968; Elbs, *J. prakt. chem.*, [2] **35** (1887), 481.

[13] Ador and Meier and Elbs in their work on dixylyl ketones did not definitely determine the positions of the methyl groups in the ketone, but appear to have assumed the structure from the reactions of the ketone and from the fact that they recovered some 1-carboxyl-2,4-dimethylbenzoic acid, during the preparation of their dixylyl ketone.

[14] Elbs (*Loc. cit.*) shows that the xylyl ketone on long heating loses a molecule of water and goes to trimethylanthracene, which on oxidation gives a trimethylanthraquinone.



M. p. 222°

To confirm these results some of the ketone obtained in the above work was gently refluxed for several days and then distilled. A pasty solid was obtained which on purifying by sublimation and recrystallizing from acetone gave a solid melting at 222° C. The yield was somewhat improved by adding zinc dust to the ketone before heating, but at best was only a little over 20 per cent. By means of chromic acid in acetic acid the trimethylanthracene was changed to the corresponding trimethylanthraquinone melting at 190°. These figures confirm results of Elbs.

American Oil Chemists' Society

The 13th Annual Meeting of the American Oil Chemists' Society will be held at the Grunewald Hotel, New Orleans, La., May 8 and 9, 1922. An unusually interesting program is being arranged and a large attendance is expected.

Notwithstanding business conditions, the American Oil Chemists' Society has made notable progress this year not only in its membership but in its extended activities.

Effect of Paraffin Wax on Viscosity of Petroleum Oils[1,2]

By E. W. Dean[3] and M. B. Cooke[4]

Bureau of Mines, Petroleum Division, Chemical Section, Pittsburgh, Pennsylvania

Experiments have been performed to determine the effect upon viscosity of changing the paraffin wax content of several petroleum oils. It was found that, as a general rule, the viscosity of any mixture is intermediate between the viscosity of the paraffin and that of the wax-free oil. That this rule is approximate rather than absolute is proved by the fact that mixtures of paraffin and an oil of practically equal viscosity were slightly less viscous than either of the constituents.

Paraffin wax, when dissolved in oil, behaves like an oil of low viscosity at temperatures considerably below its melting point.

Commercial paraffin wax is a complex mixture which can be easily resolved into fractions of differing physical properties.

A need for information on the relation between paraffin wax content and viscosity of petroleum oils was recently encountered. The lack of published figures and unsatisfactory character of the information supplied to the Bureau by individuals associated with the petroleum refining industry led to the belief that this subject had probably never been given the detailed study which it merits and therefore experiments, the results of which are recounted herein, were undertaken.

Acknowledgment is made of the assistance rendered in experimental determinations by L. E. Jackson, formerly petroleum chemist, and F. W. Lane, organic chemist, of the Pittsburgh petroleum laboratory of the Bureau. A preliminary report[5] covered the results of Mr. Jackson's work.

Scope of Investigation

The work involved measurements of the viscosities of several commercial petroleum oils before and after adding predetermined percentages of commercial paraffin, and similar tests upon two distillates specially prepared in the laboratory from crude oil, before and after removing successive portions of crystalline wax. The commercial oils used were water-white kerosene, transformer oil, spindle oil, medium automobile oil, and Liberty aero oil. All the oils and the wax used were, according to the best available information, derived from Pennsylvania crude petroleum. The laboratory distillates were also derived from Pennsylvania crude oil and were very similar in general character to crude "wax distillates" as prepared in oil refineries. The paraffin wax was a well-known brand, sold largely for household use.

Changes in wax content varied from a fraction of 1 per cent up to 10 per cent. For experiments involving the removal of wax from the laboratory distillates the percentages were necessarily odd figures. For the other tests, the quantities of paraffin added were 1, 5, and 10 per cent, respectively.

Viscosity determinations were made on each original oil and on each oil-paraffin mixture. Measurements were made on each sample at several temperatures ranging between 100° and 210° F. Results are reported in terms of kinematic viscosity for the entire series of tests, Saybolt Universal figures also being given for all products except the kerosene. The specific gravities of most of the mixtures are also reported, which makes it possible to calculate absolute viscosities if such figures are desired.

To obtain supplementary information, the several products studied were subjected to conventional physical tests. Experiments were also performed to demonstrate that commercial paraffin wax is a mixture of constituents which vary appreciably in physical properties.

Experimental

DESCRIPTION OF PRODUCTS STUDIED—The two laboratory distillates were prepared by distilling a 5-gal. charge of Pennsylvania crude petroleum in an electrically heated iron still equipped with a coil for supplying "open" steam. The primary fractions obtained by means of this "steam" distillation were redistilled in a vacuum of 40 mm., and final products obtained that came over between temperature limits of 250° to 275° C. (482° to 527° F.), and 275° to 300° C. (527° to 572° F.).

Table I—Physical Properties of Products Used in Experiments

Nature of Product	Specific Gravity at 60° F.	° Bé.	Flash Point[1] ° F.	Fire Point[1] ° F.	Saybolt Universal Viscosity at 100° F.	130° F.	210° F.
Water-white kerosene	0.795	46.1	...	...	....	....	....
Laboratory distillate[2]	0.835	....	...	...	53.8	43.4	34.3
Laboratory distillate[3]	0.847	....	...	....	69.2	50.8	36.3
Transformer oil	0.852	34.3	340	395	72.7	51.7	36.5
Spindle oil	0.883	28.6	415	480	212.7	111.0	46.8
Medium auto oil	0.883	28.6	420	470	283.0	141.0	52.0
Liberty aero oil	0.888	27.7	475	530	874.0	383.0	89.1
Paraffin wax[4]	.....	....	...	...	....	52.0	37.0

[1] Cleveland open cup.

[2] Distillation limits at 40 mm. vacuum, 250° to 275° C. (482° to 527° F.).

[3] Distillation limits at 40 mm. vacuum, 275° to 300° C. (527° to 572° F.).

[4] Melting point of paraffin wax, 126.0° F.; specific gravity at 130° F., 0.7830.

The commercial products were obtained from refining companies operating and marketing in the Pittsburgh district. The physical properties of both the laboratory and commercial products are indicated by figures in Table I.

OPERATING DETAILS—The method of separating wax from the laboratory distillates was an adaptation of the commercial process of "filter pressing" wax distillate. The actual procedure involved forcing the cooled oil through a specially designed pressure filter, the separating medium being ordinary filter paper. The quantities separated were determined by weighing the wax scraped from the filter paper after the liquid oil had been driven through. The resultant figures are, of course, only approximate, but the accuracy is sufficient for present purposes.

Additions of wax to the commercial oils were made on the basis of percentage by weight of paraffin in the mixture. Viscosity determinations were made either with the Saybolt Universal viscosimeter or with Ostwald viscosimeters. The latter instruments were calibrated so that results could be expressed in terms of either kinematic viscosity or Saybolt viscosity. The kinematic viscosity equivalents of the figures obtained by direct use of the Saybolt viscosimeter were calculated by means of the familiar Bureau of Standards equation.[6] Results for all oils except the kerosene are reported in terms of both systems of viscosity units.

Discussion of Results

Results of the principal series of viscosity tests are shown in Table II.

It will be observed that the viscosity of the original oil has a marked influence on the effect of changes in wax con-

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[1] Received January 11, 1922.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Petroleum Chemist, Pittsburgh Experiment Station, Bureau of Mines.

[4] Assistant Petroleum Chemist, Pittsburgh Experiment Station, Bureau of Mines.

[5] E. W. Dean and L. E. Jackson, "The Effect of Crystalline Paraffin Wax upon the Viscosity of Lubricating Oil," *Bur. Mines, Repts. of Investigations* **2249**, May 1921.

[6] $\text{Kinematic viscosity} = 0.00220 \times \text{Saybolt viscosity} - \frac{1.80}{\text{Saybolt viscosity}}$.

TABLE II—CHANGES IN VISCOSITY CAUSED BY VARYING PARAFFIN WAX CONTENT OF SEVERAL PETROLEUM OILS

DESCRIPTION OF OIL	Percentage Change Paraffin Content of Oil	Specific Gravity at 100° F.	Saybolt Universal Viscosity at			Kinematic Viscosity at		
			100° F.	130° F.	210° F.	100° F.	130° F.	210° F.
Water-white kerosene	0	0.7800	....	....	....	0.01930	0.01415	0.00842
	+ 1	0.7805	....	....	....	0.01864	0.01446	0.00857
	+ 5	0.7810	....	....	....	0.01994	0.01532	0.00902
	+ 10	0.7812	....	....	....	0.02166	0.01655	0.00958
250° to 275° C. laboratory distillate[1]	0	....	53.8	43.4	34.3	0.0849	0.0539	0.0230
	− .5	....	(51.4)	43.5	34.3	(0.0781)	0.0543	0.0230
	−1.9	....	54.5	43.7	34.4	0.0870	0.0548	0.0234
	−2.5	....	54.7	43.8	34.3	0.0874	0.0551	0.0230
	−3.3	....	54.9	43.9	34.2	0.0880	0.0555	0.0228
275° to 300° C. laboratory distillate[1]	0	....	69.2	50.8	36.3	0.1262	0.0763	0.0303
	−1.5	....	(64.5)	50.7	36.1	(0.1139)	0.0760	0.0295
	−3.0	....	69.1	50.7	35.9	0.1260	0.0760	0.0290
	−5.9	....	68.7	50.3	35.9	0.1250	0.0749	0.0290
	−9.0	....	71.4	51.0	36.3	0.1320	0.0769	0.0303
Transformer oil	0	0.8400	69.3	51.7	36.5	0.1264	0.0789	0.0310
	+ 1	0.8391	68.3	51.5	35.9	0.1239	0.0783	0.0288
	+ 5	0.8374	67.3	51.2	35.1	0.1213	0.0775	0.0260
	+ 10	0.8353	67.5	50.8	34.5	0.1218	0.0760	0.0237
Spindle oil	0	0.8691	213	111	46.8	0.4602	0.2280	0.0642
	+ 1	0.8683	206	109	45.0	0.4445	0.2233	0.0590
	+ 5	0.8656	188	100	43.3	0.4040	0.2020	0.0537
	+ 10	0.8606	168	91.5	43.0	0.3589	0.1816	0.0527
Medium automobile oil	0	0.8703	283	141	52.0	0.6162	0.2974	0.0798
	+ 1	0.8675	257	137	50.9	0.5584	0.2883	0.0766
	+ 5	0.8581	246	128	50.4	0.5339	0.2675	0.0752
	+ 10	0.8615	215	115	48.2	0.4646	0.2374	0.0687
Liberty aero oil	0	0.8744	874	384	89.1	1.923	0.8448	0.1758
	+ 1	0.8723	826	359	87.8	1.817	0.7898	0.1727
	+ 5	0.8698	688	319	78.3	1.514	0.6962	0.1492
	+ 10	0.8650	561	272	72.5	1.234	0.5918	0.1341

[1] Some viscosity measurements for the two laboratory distillates were made at temperatures slightly different from those listed. The figures given are interpolated to permit tabulation on an equivalent basis.

tent. Addition of wax to the kerosene increased its viscosity. The change in the case of the two laboratory distillates is practically negligible. For the other four oils there is a decrease in viscosity, as a result of adding paraffin, the decrease varying with the viscosity of the original oil. For example, the maximum decrease for the transformer oil is of the order of 5 per cent and for the Liberty aero oil is of the order of 35 per cent.

The obvious conclusion is that this investigation is simply one phase of the familiar general problem of the viscosity of mixtures. The effect of the paraffin wax seems to be practically identical with what might have been expected if, instead of the wax, a liquid oil of equal viscosity had been used. Actual measurements (see Table I) showed that at temperatures above its melting point, the viscosity of the paraffin was approximately the same as that of the transformer oil. When mixed with the more fluid kerosene it caused an increase in viscosity, and when mixed with the more viscous oils there was a decrease.

The transformer oil and the two laboratory distillates might seem to be exceptions to the simple qualitative rule that holds for the other products. The wax and transformer oil are practically equal in viscosity, and the mixtures are less viscous than either of the constituents. This occurrence, though interesting, is not at all surprising, as the viscosities of oil blends are usually less than the values calculated by the most satisfactory rule for additivity.[7]

There is a more definite explanation for the results obtained with the two laboratory distillates. Neither of these products showed appreciable changes in viscosity when various percentages of paraffin were removed. These two oils were considerably different in viscosity, and as a logical inference it was to be expected that the properties of the paraffin removed from one distillate would not be identical with those of the paraffin removed from the other. The separated paraffin, unfortunately, was not retained, and this probability could not be investigated by direct experimentation.

It was shown, however, that the wax used in the other tests could be resolved without difficulty into fractions of differing physical properties. To determine this experimentally a 15-g. sample of paraffin was dissolved in 7.5 g. of pure benzene by warming to a temperature of approximately 60° C. The solution was then cooled to 30° C., and the resulting crystals of wax were removed by filtration. The benzene was then removed from both "precipitate" and "filtrate" by evaporating for 3 hrs. on a steam bath. The yield of paraffin from the precipitate was approximately 7 g., while that from the filtrate was 8 g. The properties of the original paraffin and of the two fractions are indicated by the figures in Table III.

TABLE III—SHOWING THAT COMMERCIAL PARAFFIN WAX IS A MIXTURE OF CONSTITUENTS HAVING VARYING PHYSICAL PROPERTIES

NATURE OF MATERIAL	Melting Point ° F.	Saybolt Universal Viscosity at 150° F.
Commercial paraffin	126	44
Fraction separating at 30° C. from a solution of 2 parts by weight of paraffin in 1 part by weight of benzene	132	46
Fraction remaining in solution at 30° C. when 2 parts of paraffin were dissolved in 1 part of benzene	119	42.5

It will be noted that even so simple a method of separation as this shows that commercial paraffin wax is a mixture of constituents of differing physical properties. Such being the case, it is entirely justifiable to assume that the paraffin separated from the laboratory fraction distilling between the limits of 250° to 275° C. is less viscous than that separated from the 275° to 300° C. fraction.

It has been impossible to formulate a quantitative rule for the effect of varying the paraffin wax content of oil from the figures in Table II. In a majority of cases the decreases or increases in viscosity are of such size as to be somewhat influenced by normal experimental errors in the determinations; furthermore, there is no satisfactory general rule for calculating the viscosity of blends. The method outlined by Herschel[7] is admittedly only an approximation, and is particularly unsatisfactory for mixtures in which the relative percentages of constituents are so different.

One of the most interesting facts brought out by these experiments is that, when dissolved in oil, paraffin wax seems to behave like an oil of low viscosity at temperatures appreciably below its melting point. Its effect upon viscosity at 100° F., which is 26° F. below its melting point, is similar to its effect at 130° and 210° F. The temperatures at which the oil-wax mixtures would begin to deviate from the general—though perhaps indeterminate—rules covering the viscosity of blends were not determined, but it seems safe to assume that they are related to the so-called cloud points, or points at which solid paraffin begins to separate.

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[7] W. H. Herschel, "Saybolt Viscosity of Blends," *Bur. Standards, Technologic Paper* **164** (1920).

Notes on the Chemistry of Lime Liquors Used in the Tannery[1]

By W. R. Atkin

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The following paper describes an extension of the theories of Procter and Wilson and of Loeb to the alkaline swelling of hide in lime liquors. The real reason why such "sharpening" agents as sodium sulfide and sodium carbonate produce greater swelling is that the osmotic pressure of sodium collagenate is greater than that of calcium collagenate at the same hydrogen-ion concentration. The smooth grain of skins unhaired by arsenic sulfide is due to the fact that only calcium collagenate is produced. A rapid method for the analytical control of lime liquors by swelling experiments on hide powder is described. Alkaline swelling is shown to be exactly analogous to acid swelling, which has been much more extensively investigated, and certain tanning processes are shown to act in a parallel way to acid pickling.

The process of liming consists of soaking softened hides or skins in alkaline liquors, generally containing lime, for the purpose of rendering the hair loose so that it may be scraped off by means of an unhairing knife or machine. The unhairing action is generally supposed to be due to solution of the *rete malpighi* by the action of alkalies, sulfides and enzymes secreted by bacteria which are able to function even in such strongly alkaline liquors. Simultaneously with this action there occurs a swelling or plumping of the fibers which has a pronounced effect upon the nature of the final leather. The object of this paper is to present an explanation of the different swelling effects produced by varying the procedure of liming.

Stiasny[2] differentiates between plumping and swelling, but as the degree of plumping is not an easily measurable quantity, our work was confined to measurements of swelling. Plumping will be studied later.

In practice lime liquors are generally "sharpened" to increase the rate of unhairing by the addition of such substances as sodium sulfide, arsenic sulfide, and sodium carbonate. The sodium salts increase the alkalinity of the liquors through the formation of sodium hydroxide and there is an increased plumping of the skins. Stiasny has shown that the conditions favorable to rapid unhairing are obtained when the proportion of sodium hydroxide to sulfhydrate is unity. Sodium sulfhydrate exerts a strong solvent action on the keratinous matter. When red arsenic sulfide is used, it is slaked with the lime and the resulting solution is found to unhair quickly, but without increased plumping or swelling of the skins. Stiasny has shown that the unhairing action is due to the formation of calcium sulfhydrate and that the arsenic plays no important part, merely being converted into calcium sulfarsenite. Chrome tanners use this mixture because it causes goat skins for glacé kid to have a smoother and silkier grain when finished.

Theoretical Considerations

In order to obtain a good working knowledge of the theory of the swelling of hides and skins in alkaline solutions, it is necessary to understand the work of Procter,[3] Procter and Wilson,[4] and Loeb,[5] who have studied the action of acids, alkalies, and salts upon gelatin. The swelling of gelatin in acids or alkalies is due to the formation of an ionizing salt, such as gelatin chloride, and as the gelatin ion is nondiffusible, the acid-treated gelatin may be likened to an osmometer—the outer solution passing into the jelly until equilibrium is attained. Gelatin is an amphoteric substance; its isoelectric point is at pH = 4.7, corresponding to a hydrogen-ion concentration of $10^{-4.7}$ *N*. At any higher pH the gelatin is an equilibrium mixture of isoelectric gelatin and metal gelatinate, whereas at any pH lower than 4.7 there is a mixture of isoelectric gelatin and gelatin-acid salt.

Since collagen is very closely related to gelatin it would be expected to behave like gelatin, just as do other proteins such as egg albumin and casein. This has been found to be the case, and experiments at Leeds have shown the isoelectric point of collagen (or hide powder, which is the nearest approach to pure collagen we have) to be at a pH of about 4.8, which is almost identical with that of gelatin.

Loeb has shown that such properties as swelling, osmotic pressure, and viscosity depend on the hydrogen-ion concentration in the swollen protein. As the outer solution of acid or alkali is in equilibrium with the protein, these properties therefore depend also on the hydrogen-ion concentration of the outer solution, provided we are dealing with solutions of acids or alkalies alone. The addition of salts introduces further complications. The writer[6] has shown by calculations based on the theory of protein swelling put forward by Procter and Wilson that the results of these workers agree remarkably well with the results of Loeb and of Miss D. Jordan-Lloyd,[7] although the methods of experiment differed greatly in character. The results obtained by the above workers show that at pH = 2.4 for the outer solution of acid in equilibrium with gelatin (corresponding to pH = 3.0 in the jelly) a maximum swelling is attained with such acids as hydrochloric, nitric, phosphoric, tartaric, citric, acetic, and formic—this maximum being practically the same for all the different acids. Sulfuric acid also shows a maximum at the same pH value, but in this case the swelling is only about half that in the case of the other acids mentioned. Loeb explains this fact as follows: Hydrochloric, nitric, and phosphoric acids, etc., behave as monobasic acids forming salts of the type Gel-Cl, Gel-NO_3, but sulfuric acid acts as a dibasic acid, forming $(Gel)_2SO_4$. If we have equivalent quantities of the chloride and the sulfate at the same pH, the swelling is proportional to the osmotic pressure and that of the gelatin ion is negligible; hence the osmotic pressures are proportional to Cl^- and $^1/_2\,SO_4^{--}$. It is clear that the chloride swells more than the sulfate, roughly in the ratio of 2 : 1.

Similarly, sodium, potassium or ammonium gelatinate would swell more at corresponding pH values than would the salts of calcium or barium.

Experiments on Hide Powder

In order to test whether such reasoning could be applied to collagen the following experiments were carried out:

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[1] Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] *Gerber*, **1906**; *J. Soc. Leather Trades' Chem.*, **3** (1919), 129.

[3] *Kolloidchem. Beihefte*, **2** (1911), 243; *J. Am. Leather Chem. Assoc.*, **6** (1911), 270; *J. Chem. Soc.*, **105** (1914), 313.

[4] *J. Chem. Soc.*, **109** (1916), 307.

[5] *J. Gen. Physiol.*, **1918–1920.**

[6] *J. Soc. Leather Trades' Chem.*, **4** (1920), 248, 268.

[7] *Biochem J.*, **14** (1920), 147.

Half-gram lots of Standard hide powder were weighed out into 100-cc. graduated flasks, which were then filled up to the mark with different concentrations of solutions of sodium, barium[8] or calcium hydroxide which had been prepared with CO_2-free distilled water. The flasks were corked and left for 24 hrs. in an incubator at 25°. The corks were then replaced by pieces of rubber tubing closed by a spring clip in the middle. The other end of a rubber tube was connected to a buret sealed at the bottom and containing sufficient mercury to come up as far as the scale divisions. After the inverted flask was connected to the buret, the spring clip was slipped off and the swollen hide powder was allowed to settle down into the buret. The flask was shaken occasionally in order to collect all the hide powder in the buret and after 3 hrs. the volume of powder was read off from the buret. The equilibrium alkaline solution was filtered and an aliquot portion titrated. By means of tables the pH values were calculated, allowing for the different degrees of dissociation of the different alkalies. The volume of the swollen hide powder corresponded to the swelling.

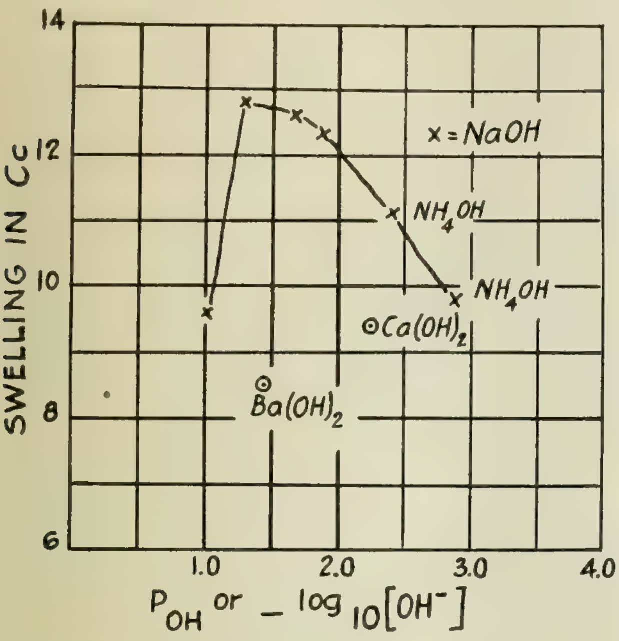

Fig. 1

Similar experiments were carried out with sodium hydroxide and calcium hydroxide, in solutions which were also made 0.05 *M* in $BaCl_2$ and 0.1 *N* in NaCl.

The results of the experiments are given in Tables I and II.

Table I

Normality of Equilibrium Solution		Equivalent to pH Value of	Swelling of Hide Powder, Cc.
$Ba(OH)_2$	0.0405	12.55	8.5
$Ba(OH)_2$	0.016	12.11	7.9
$Ba(OH)_2$	0.007	11.81	9.7
$Ba(OH)_2$	0.0025	11.38	9.7
$Ca(OH)_2$	0.006	11.75	9.4
NaOH	0.113	12.99	9.6
NaOH	0.055	12.70	12.8
NaOH	0.022	12.31	12.6
NaOH	0.014	12.12	12.3
NH_4OH	0.865	11.60	11.1
NH_4OH	0.0935	11.11	9.8
Distilled water		6.4	5.85

The addition of salt to the alkali-swollen collagen effects a repression of swelling exactly as in the case of pickling, when salt produces a remarkable falling effect on acid-swollen skins. Doubtless, the repression would be greater with more concentrated salt solutions, but it is distinctly perceptible with 0.1 *N* NaCl.

Table II

Final pH	Swelling Cc.	Final pH	Swelling Cc
$Ba(OH)_2$ plus $BaCl_2$ (0.1 *N*)		$Ba(OH)_2$ plus NaCl (0.1 *N*)	
12.55	6.9	12.56	10.1
12.13	7.5	11.81	11.0
11.84	8.4	11.46	10.8
11.46	8.7		
NaOH plus NaCl (0.1 *N*)		NaOH plus $BaCl_2$ (0.1 *N*)	
12.68	10.8	12.65	8.1
12.27	11.6	12.29	8.8
11.98	12.3	11.83	10.2

The results recorded in Table II are easily explained by the Procter-Wilson theory and show that alkaline swelling is governed by the same laws as acid swelling.

The results obtained upon adding sodium chloride to the barium hydroxide solutions and barium chloride to the sodium hydroxide are also given in Table II. Although neutral salt has a tendency to repress swelling, we find here that the mixture of sodium chloride with barium hydroxide produces more swelling than does barium hydroxide alone and also that barium chloride produces a bigger depression than an equivalent amount of sodium chloride, if added to collagen swollen with caustic soda. These results confirm for collagen the conclusions arrived at by Loeb for the action of alkalies on gelatin. In the experiments mentioned above we are really dealing with a reversible reaction of the type

$$Ba^{++}\ (Coll)_2^- + 2Na^+\ Cl^- \rightleftharpoons 2\ Na^+\ Coll^- + Ba^{++}\ Cl_2^-,$$

the relative proportions of the four constituents being governed by the law of mass action.

The addition of sodium chloride to barium collagenate tends to form sodium collagenate which has a bigger swelling capacity. Where barium chloride is added to collagen swollen with sodium hydroxide (sodium collagenate) the barium collagenate formed has a lower swelling power and the swelling is further depressed by the neutral salt present.

Application of Theory to Tanning Practice

This extension of the Procter-Wilson-Loeb theory to the alkaline swelling of hides provides explanations for several phenomena that have been described by various workers and also for some practical and empirical methods used by tanners.

ARSENIC SULFIDE—Probably the most important of these is the use of arsenic sulfide already mentioned. Despite the high cost of this substance it is preferred by chrome tanners for liming skins for glacé kid because of the smooth grain obtained. It is obvious that if a skin is excessively swollen during the preliminary stages of leather manufacture the grain will tend to become rough and coarse. Stiasny has shown that the use of arsenic sulfide is dependent on the production of calcium hydrosulfide, together with calcium sulfarsenite. The consequence is that only a calcium collagenate swelling takes place, and this is repressed to some extent by the soluble calcium sulfarsenite produced.

SODIUM SULFIDE—If, however, the cheaper sodium sulfide were used sodium hydroxide and hydrosulfide would be produced and the swelling would then be partly due to sodium collagenate and therefore greater. This effect would be further increased by the addition of more hydroxide ions arising from the hydrolysis of the sodium sulfide and consequent precipitation of some calcium hydroxide to keep the solubility product of the latter constant. Thus the addition of sodium sulfide to lime gives rise to a distinct increase of swelling compared with lime alone and still greater than that produced by lime and arsenic sulfide. This increase of swelling would explain the coarser grain obtained by the use of sodium sulfide. Procter's suggestion that the addition of calcium chloride would permit the use of sodium sulfide for unhairing skins even for this delicate work is thus seen to have a sound theoretical basis. Guisiana has suggested a similar procedure. It will be noticed by reference to Table I that an increase of alkalinity from 0.05 *N* (which is approximately the strength of saturated lime water) to 0.1 *N* (or a rise of pH from 12.70 to 13.0) does not produce any increase in swelling but rather the reverse. In practice, however, if a lime liquor be strengthened with sodium sulfide or sodium carbonate, the hides or skins will be found to be much more plumped or swollen. This increased swelling was formerly thought to be due to the increased alkalinity, but it would seem more in accordance with the true facts of the case to ascribe it to the increased swelling due to sodium collagenate. Here, again, some calcium hydroxide would be forced out of solution by the increased alkalinity. The present writer and his collaborators[8] have proposed two methods for the determination of the caustic alkalinity of lime liquors, but in view of these results the simplest control of lime-yard liquors would be to carry out swelling experiments on hide powder exactly as described in this paper. The swellings could be plotted against pH values and in this way successive liquors could be checked and a graphical record preserved.

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[8] Barium hydroxide has been used on account of its greater solubility, but a reference to Table I will show that calcium hydroxide gives practically identical results. Any conclusions arrived at for barium hydroxide or barium chloride will apply to calcium hydroxide or calcium chloride.

WASHING OF HIDES—It has been the custom of many sole leather tanners to wash out practically all the salt in the hides before they are limed. Reference to Table II will show that the presence of sodium chloride causes more swelling of barium collagenate than when barium hydroxide alone is used. The same effect will be shown with calcium collagenate. The sole leather tanner can use as a sharpening agent to promote swelling and plumping, the salt that is already present in the hides and need not wash it out before liming. This method of working has been used with success in a large sole leather yard in England.

The reason why such care has been taken by tanners to remove salt from the hide appears to be the fear that salt may be carried forward to the tan pits and produce a flat empty leather. The employment of the three-pit system of liming and subsequent deliming would remove practically all the salt before the hides went forward to the tan liquors.

AMMONIUM HYDROXIDE—An interesting confirmation of the results given in this paper was described by Stiasny. Calf skin with the hair on was soaked in 200 cc. of liquor consisting of 0.5 *N* ammonium hydroxide to which equivalent quantities of various chlorides had been added: 0.84 g. NaCl, 0.8 g. $CaCl_2$, or 1.76 g. $BaCl_2$ (Table III).

TABLE III—WEIGHT ABSORPTION (PER CENT) WITH VARIOUS CHLORIDES

	NH_4OH	NH_4OH + NaCl	NH_4OH + $CaCl_2$	NH_4OH + $BaCl_2$
After 1 day	58.6	37.4	15.5	14.1
After 2 days	65.5	45.8	14.9	19.8

The pickling effect of the salts was apparent in each case but the repression of swelling was much greater with barium and calcium chlorides. In the case of ammonia and ammonia plus sodium chloride the hair was quite loose after 4 days, but not in the cases where calcium or barium chloride was used. Stiasny suggested that the explanation might be due to the formation of complex ammonia compounds of the type $Ca(NH_3)_8Cl_2$, but it has been shown by J. Atkin and the writer[9] that the hydroxyl-ion concentration of ammonia solutions is not altered by the addition of sodium chloride or calcium chloride. The explanation of the differences in swelling is of course exactly the same as for the results given in Table II, but the differences in unhairing capacity seem to require further investigation.

Effect of Concentration of Salts

The influence of salt solutions of various concentrations on gelatin has been investigated by H. R. Procter, who found that increasing concentrations of salt caused an increased swelling; this, however, attained a maximum and afterwards fell on increasing the concentration of the salt solution.

Commercial gelatin appears to be almost always on the alkaline side of the isoelectric point and really contains some calcium collagenate, as the ash always contains calcium. By treatment with sodium chloride the following equilibrium is set up:

$$Ca(Coll)_2 + 2NaCl \rightleftharpoons 2NaColl + CaCl_2,$$

the sodium collagenate causing an increase of swelling. Higher concentrations of salt then cause a depression of swelling.

Meunier[10] found that potassium carbonate solutions of high concentration completely dehydrate pelt and yield a leather which is wet back into pelt on treatment with water. The action may be explained on similar grounds to the above: the production of potassium collagenate and the pickling effect of the excess potassium carbonate. Meunier, however, showed that a permanent leather could be obtained by using potassium carbonate together with formaldehyde in 0.3 per cent solution.

McLaughlin[11] has published two papers dealing with the swelling of pelt in acids, one using limed pelt and the other with fresh pelt. The results are vitiated, however, by the facts that in the first paper no allowance was made for the lime in the pelt and the consequent buffer action of the calcium salts dissolved out by the acids and also that the concentrations of the acids are given only in terms of normality by titration and the normality so stated is that before equilibrium has been set up. It is well known that hide, like gelatin, takes up a certain amount of acid and therefore the concentration of the residual acid *after equilibrium* should be determined. Further, Loeb's work has shown that comparisons of swelling are only valid if made at the same hydrogen-ion concentration, but McLaughlin makes no determinations of this; furthermore, it is not possible to calculate it from the dissociation constants of the acids for the reasons given above. It is very much to be regretted that so much painstaking work has been to a large extent nullified by these omissions.

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[8] *J. Soc. Leather Trades' Chem.*, **4** (1920), 111, 236, 248, 268.

[9] *Ibid.*, **4** (1920), 236.

[10] *Collegium*, **1912**, 11, 54, 420.

[11] *J. Am. Leather Chem. Assoc.*, **15** (1920), 228; **16** (1921), 295.

The International Chemical Conference

The general program of the Third International Chemical Conference, to be held at Lyons, France, June 27 to July 2, inclusive, includes meetings of the Council, reports of committees and visits to factories in the vicinity. On July 2, the delegates will go down the Rhône by boat to the neighborhood of Marseilles, where they will have an opportunity to attend the second congress of industrial chemistry, which has been arranged by the Société de Chimie Industrielle.

This congress will be held July 2 to 7. Among the general questions which will be considered are the animal, vegetable, and mineral resources of the French colonies. In addition to this, fats, soaps, etc., will be discussed.

Professor Moody Succeeds Professor Baskerville

On March 27, Prof. Herbert R. Moody, for seventeen years connected with the Department of Chemistry of the College of the City of New York as Professor of Industrial Chemistry and Chemical Engineering, was unanimously appointed to the Directorship of the Department to fill the vacancy caused by the death of Prof. Charles Baskerville.

Lye Hominy: Its Discoloration and a New Process for Its Manufacture[1]

By **Edward F. Kohman**

Research Laboratory, National Canners' Association, Washington, D. C.

The discoloration of canned lye hominy is apparently the result of alkalinity, due to incomplete washing of the hominy. When alkali is added to the water used in canning, typical blackening occurs in a short time. Acid, however, cannot be added to counteract the blackening, because it causes starch to settle out, and produces too hard and solid grains.

Repeated washing produces no appreciable effect on alkalinity after the first washing. The length of time of lying does affect the alkalinity of the product, the pH value varying from about 6.50 for a 10-min. lying period to about 9.00 for a 50-min. period.

Other factors affecting the alkalinity are size and shape of grain. In general, a thin, flat, small grain will yield a more alkaline hominy than a large, thick grain. Treatment of the corn with hot or cold water before lying slightly decreases the alkalinity of the product, but drying of the corn in vacuo has no noticeable effect. The age of the corn has a marked effect on its behavior in hominy making. The hulls are more easily removed from old corn, and it consequently acquires a greater degree of alkalinity. On the other hand, the tips are less easily removed.

To prevent the formation of black discoloration, the pH value of lye hominy should be reduced as low as possible by ample washing with boiling water or even at higher temperatures under pressure. In the following paper there is described a scrubbing or abrasion process to be applied directly after lying, by means of which the outer layer of the grain may be removed. This treatment materially lowers the alkalinity; aids in removing the tips and bran layer, thus making possible a shorter lying process with a consequent lowering of pH and removes the outer layer, which was colored by the lying process, giving a hominy of pleasing white appearance. All other attempts to lower the pH value resulted in a less complete removal of tips and bran layer.

In the study of discoloration that occurs in canned corn, a tendency was observed for the corn showing the greatest discoloration to have a lower acidity, as determined by titration. It was thought, therefore, that the black discoloration of hominy might be due to some of the lye not being washed out. The resulting alkalinity would render the sulfur-bearing proteins less stable and favor the formation of hydrogen sulfide, and would also favor the precipitation of the low concentration of ferrous sulfide which is the black discoloring agent.

Accordingly, in March 1920, a pack of hominy was put up under commercial conditions with water containing, respectively, 10, 15, and 20 cc. 0.1 *N* sodium hydroxide per 100 cc., and also 10, 15, and 20 cc. 0.1 *N* hydrochloric acid per 100 cc., respectively. Within a few days a few grains against the junction of the body and end of the can containing even the smallest amount of alkali showed the black discoloration but the control remained normal. This gradually became more pronounced so that within a year the liquor became dark and a number of grains were black almost throughout. The pH value of the control hominy was 7.12; that of the hominy containing 10 cc. 0.1 *N* alkali per 100 cc. liquor was 8.06.

As the control did not develop any black even after more than a year, the effect of the addition of acid in preventing it, if any, could not be demonstrated. But another very marked effect of the acid should be noted. The starch seemed to settle to the bottom and formed a solid cake during processing which extended nearly half way up in the can. Moreover, the loose grains above it were of a rather firm and solid texture as compared with normal hominy. This phenomenon was observed in similar experiments carried out later, thus demonstrating the impossibility of using acid to counteract black formation.

In December 1920, a second pack was put up in another plant, in which 1, 2, and 4 cc. 0.5 *N* sodium hydroxide, respectively, were added per 100 cc. of water used for canning. Typical black began to form within a short time and gradually increased, while the controls were still free from black. For comparison with data given below, it should be stated that the pH of those packs were as given in Table I. All values for H-ion concentration recorded in this paper were determined on the hominy liquor by the electrolytic method.

Table I—Effect of Alkali on Black Formation

Cc. 0.5 *N* NaOH added per 100 cc. H_2O	0	1	2	4
pH value	7.0	7.39	7.76	8.58
Black formation	−	+	+	+

Effect of Washing on pH Value

To duplicate commercial conditions a pack was put up at the same time in which the amount of washing that the hominy received was varied. After lying, the hominy was run once through a Sprague brushing machine and then through a squirrel cage while cold water was being sprayed on to it. Then it was given nine 15-min. washings in the usual hominy tubs. In one experiment the washing was done with cold water. In the other, the water was brought to boiling each time. This required about half of the 15 min., so that in each washing the corn was treated for only about 8 min. with actually boiling water. Samples taken after each washing were canned. Contrary to expectations, the successive washings produced no appreciable effect on the alkalinity even from the first washing. The pH is given in Table II.

Table II—Effect of Washing on pH Value

Sample No.	1	2	3	4	5	6	7	8	9
Cold washed	7.12	7.08	6.96	6.94	6.96	6.88	7.02	6.88	6.93
Hot washed	7.01	6.94	6.84	6.87	6.91	6.84	6.94	7.04	6.78

Two similar experiments with the same corn at the same plant gave the results closely duplicating the above.

So low a pH in commercial hominy is unusual. A sample of hominy from the same plant but of a previous year had a pH of 7.88. Only one other brand has come to the writer's attention in which the pH was below 7.0, whereas the average pH for commercial hominy is 7.5 or above. This was new-crop corn and the moisture content was still so high that the shelled corn did not "flow" smoothly but tended to "bank." It was thought that in this condition the hulls might be removed by a materially less severe lying process, with a consequently lower pH. The effect of the age of the corn will be discussed below.

To get a clearer insight into the effect of the washing process in making lye hominy, the following laboratory experiment was made. A 2100-g. sample of corn was lyed by boiling for 25 min. in 7 l. of lye solution containing 52.5 g. of sodium hydroxide. This is the equivalent of 1 lb. 85 per

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[1] Received November 9, 1921.

cent lye per bu. The hominy was dumped on a sieve and the lye solution rinsed off with a stream of cold water. Next 160-g. samples were weighed into 14 No. 2 cans. Half were filled with boiling distilled water and half with boiling tap water and all boiled in a calcium chloride bath. After 15 min. 6 cans of each lot were drained and again refilled with boiling distilled and tap water, respectively. After the next 15-min. period only 5 of each lot were so drained and refilled, etc., until there was only one can of each lot for the sixth draining. In this way all cans were cooked the same length of time but varied in the amount of washing they received. All were closed, cooked for 1.5 hrs. at 212° F., and finally for 70 min. at 240° F. (116° C.). Table III gives the results obtained upon examination of the cans the next day.

TABLE III

	Wt. Ash of 25 Cc. Filtered Liquor		0.1 *N* Acid Required to Neutralize Ash (Methyl Orange Indicator)		pH Value	
Times Drained	Distilled Water Grams	Tap Water Grams	Distilled Water Cc.	Tap Water Cc.	Distilled Water	Tap Water
0	0.0434	0.0432	4.40	3.95	7.84	7.82
1	0.0348	0.0338	3.15	2.80	7.57	7.56
2	0.0272	0.0285	2.35	1.95	7.44	7.61
3	0.0242	0.0248	1.90	1.60	7.38	7.28
4	0.0218	0.0217	1.70	1.35	7.38	7.54
5	0.0189	0.0223	1.40	1.30	7.37	7.50
6	0.0177	0.0200	1.30	0.90	7.43	7.48

It is apparent that after the first draining there is no consistent drop in the pH. There is, however, a gradual decrease in the weight and alkalinity of the ash of the liquor with each succeeding washing. Two plausible explanations may be offered in this connection. First, hominy presents a buffer mixture and as the alkali is washed out, the buffer is also washed out. This amounts to the same thing as dilution of a buffer solution which does not have its pH changed thereby. Second, the protein or other difficultly soluble material in the grain may have its pH altered during the lying process; such products would be washed out extremely slowly and yet might be soluble enough to affect the reaction of the liquor.

EFFECT OF INTENSITY OF LYING PROCESS

In view of the above results, it was necessary to find elsewhere the cause for the great variation in pH observed in different brands of commercial hominy. One very important factor causing such variation in the reaction of hominy is the length of the lying period. The following experiment will illustrate. The corn was lyed in the usual way, and samples of equal weight were removed from the lying bath after 10, 20, 30, 40, and 50 min. Each sample was rinsed three times with about three times its weight of cold water. Each sample was then divided into three equal portions: the first was given one 15-min. cook, drained, then canned, and given a 150-min. cook at 212° F.; the second was given two 15-min. cooks, drained after each, then canned, and given a 135-min. cook; the third was given three 15-min. cooks, drained after each, then canned, and given a 120-min. cook. All were then processed at 240° F. for 70 min. in No. 2 cans. Thus all samples were cooked 165 min. at 212° F., and 70 min. at 240° F. after lying.

Table IV shows the effect of the different lying periods and the effect of subsequent washing or boiling out with water on the pH and on the titratable acidity and the alkalinity of the soluble ash.

The pH varies from about 6.50 for the 10-min. lying period to about 9.00 for the 50-min. lying period. Washing with boiling water has no appreciable effect on the pH, but it does decrease the titratable acidity of the liquor and the alkalinity of the soluble ash.

TABLE IV

Lying Period Min.	Times Boiled Out and Drained	0.1 *N* Alkali or Acid Required to Neutralize 100 Cc. Liquor (Phenolphthalein Indicator) Cc. Alkali	Cc. 0.1 *N* Acid Required to Neutralize Soluble Ash from 100 Cc. Liquor (Methyl Orange as Indicator)	pH Value
10	1	3.70	7.60	6.55
10	2	3.50	6.80	6.51
10	3	2.00	6.00	6.56
20	1	2.00	7.60	7.16
20	2	2.00	6.40	7.19
20	3	1.60	5.80	7.03
30	1	0.80	7.40	7.85
30	2	1.00	6.00	7.84
30	3	1.00	5.00	7.69
40	1	0.00	9.40	8.66
40	2	0.40	6.20	8.53
40	3	0.60	5.40	8.38
		Cc. Acid		
50	1	0.30	9.60	9.02
50	2	0.20	7.20	9.05
50	3	0.10	4.80	9.05

A similar experiment was made on a scale large enough to give a dozen cans of hominy for each lying period, with the idea of holding these cans to note the effect of the higher pH due to longer lying on black discoloration. The lowest pH of this experiment was 7.2 and the highest 8.2. No appreciable black had formed in four weeks, but after six weeks the hominy with the higher pH showed a number of discolored grains in the bottom of the can.

SIZE AND SHAPE OF GRAIN

There are a number of other factors which more or less influence the alkalinity of hominy. The size of the grain has an appreciable effect. From one lot of corn 200 g. of large grains and 200 g. of small grains were picked. Both were lyed alike and treated alike in other ways throughout the process. The hominy from the large grains had a pH of 7.66, whereas that from the small grains had a pH of 7.98. In general, a thin, flat, small grain will yield a more alkaline hominy than a large, thick grain.

MOISTURE CONTENT OF CORN

If the corn is treated with hot or cold water previous to lying (for example, with boiling water for 5 min. or cold water for 1 hr.) the alkalinity of the hominy is slightly less than when the corn is not so treated. The corn absorbs some water during this process which would tend to dilute the lye solution. But the above statement holds true even if the lye solution used for the unsoaked corn is diluted with an amount of water equivalent to that absorbed by the soaked corn. But the hulls are distinctly less removed in the case of soaked corn. Therefore, a longer lying period or more concentrated lye would be necessary to remove the hulls completely, and this would render the corn more alkaline. Apparently the water absorbed during the soaking period forms a protection against the penetration of the lye. Presumably the hot water forms a gelatinous coat of starch paste which acts in this manner.

Corn has been dried *in vacuo* at a low temperature before lying. In one case it lost 1.75 per cent moisture and in another case 3 per cent. In neither case was there any appreciable effect on the pH value of the hominy.

AGE OF CORN

In Table V are given the results obtained with old and new corn in January 1922. The new corn was from the 1921 crop and was raised from the seed selected from the crib from which the old corn was taken. The old corn was from the 1920 crop. In each case, 200 g. were lyed in 400 cc. of lye solution containing 5 g. of sodium hydroxide.

A very distinct difference in the behavior of the new and old corn is not brought out in Table V. On lying the old corn, the solution becomes much thicker or more viscous. This is also true of the wash water during the precook. The hull or bran layer is removed from the old corn by a shorter lying process, although the reverse is true of the tips, as is seen from the table. The old corn becomes darker in color, the germs become detached from the grains, which then tend to break. In Expt. I, when the lying period was 26 and 29 min., no count of the tips could be made for the old corn because so many grains were broken. This corn was distinctly overlyed. The old corn seemed to give a bigger swell, but there were so many inconsistencies in the different experiments that no definite figure can be given. All these differences between old and new corn are greatly diminished when the scrubbing process is used. This process overcomes the effect of overlying, and with it the old corn yielded a good hominy when lyed 26 or 29 min.

TABLE V EFFECT OF AGE OF CORN

	Expt. I Hominy not "Scrubbed"				Expt. II Hominy "Scrubbed"			
	pH Value		Per cent of Grains Still Having Tips on		pH Value		Per cent of Grains Still Having Tips on	
Minutes Lyed	New Corn	Old Corn	New Corn	Old Corn	New Corn	Old Corn	New Corn	Old Corn
20	7.41	7.98	31	47	7.20	7.55	18	28
23	7.60	8.40	24	36	7.26	7.84	9	18
26	8.00	8.69		.	7.51	7.95	8	13
29	8.08	8.55		.	7.73	8.07	7	8

EFFECT OF ALKALINITY, HYDROGEN SULFIDE, AND IRON

A separate lot of hominy was made from each of a number of ears of good seed stock corn, selected from a large crib. The procedure was uniform for each. After the lying process each lot was rinsed with uniform amounts of cold water and dumped on a sieve where it was rubbed with the hand to remove more completely the surface softened by the lying process. The effect of such a procedure on the pH will be discussed later, but at the time this effect was not realized and a variable was thus introduced in the making of these separate lots. The hominy was again uniformly rinsed and given four 20-min. cooks in boiling water. One hundred grams of each lot were canned in No. 1 flat cans. Also 25 g. were put up in each of two glass test tubes about 1 in. in diameter, by sealing off the open end. Into each of the tubes for each ear was also introduced a strip of tin plate about $^5/_8$ in. wide and long enough to extend about $^3/_8$ in. above the liquor. This strip of metal was cut from a large piece of tin plate and thus the raw cut edges were exposed to the hominy. At the same time the iron was determined on the dry corn, the pH value of the resulting hominy, and also the hydrogen sulfide evolved upon heating the hominy at 120° C. for 45 min., at that stage of its preparation when it was ready to be canned. The method for this determination is to be described in a separate paper. The samples thus used were afterward canned in No. 1 flat cans, and are discussed below.

The corn put up in the glass tubes has been observed frequently and the extent of black discoloration recorded. In the tubes where this occurred there were in nearly all cases some signs of discolored grains within a very few days after packing. These samples of hominy were all put up between April 28, 1921, and May 20, 1921. The results up to the present time may be summarized as follows: Among those samples having the highest pH, more are discolored and the discoloration is decidedly worse than among those with the lower pH. The discoloration is in the order of the amount of hydrogen sulfide formed. The discoloration is also in the order of the iron content but the relation in this respect is not so marked. These results are in harmony with the fact that alkali, and to a less extent iron salts, hastens the breaking down of sulfur-bearing proteins, with the development of hydrogen sulfide.

It is apparent from an examination of these tubes of hominy that the iron to unite with the hydrogen sulfide must come from the tin plate. In every case its development began where the grains were in contact with the cut edge of the strip of plate. In no case was any sign of black formation found in the tubes containing no tin plate. This is also borne out by the data of Table VI, which gives the iron content of the germ and endosperm, based on dry weight, of commercially canned hominy. These figures are many times greater than the iron content of normal corn.

TABLE VI

Sample No . .		1	2	3	4	5	6	7	8	9	10	11
Mg. Fe per kilo on dry basis	Endosperm	185	39	119	18	13	17	14	64	212	62	75
	Germ	5970	441	5460	501	368	1515	902	503	6670	1605	3160

EFFECT OF TEMPERATURE OF PRECOOK

In the cans containing the hominy which had been used for the hydrogen sulfide determination (*i. e.*, which had had an additional 45-min. precook at 120° C. with live steam passed through it) the tin plate was decidedly brighter than in the cans containing the hominy treated only in the ordinary way. Such a procedure would be expected to lessen the tendency to black discoloration, in that it removes some of the hydrogen sulfide and is an efficient washing. A precook at 120° C. gave a much better swell and a better appearing hominy than the 100° C. precook. It enabled one to obtain more uniform fills, inasmuch as the swell was fairly complete before canning. A uniform fill is an important consideration from the standpoint of black formation. If the can is so full as to pack the hominy firmly against the walls, the hominy is more prone to discoloration than when loosely packed. Storing cans on the side is beneficial because the weight of the hominy does not pack the lower grains so firmly against the can.

It should not be inferred that a high precook would make unnecessary the usual number of washings with hot water. These are important in the prevention of black, even though they have no marked effect on the H-ion concentration. This is evident from Table I, where it is seen that there is abundant black formation when there is only enough sodium hydroxide present to produce a pH of 7.39.

EFFECT OF SCRUBBING

In seeking for ways to keep the pH as low as possible during the process of lying, it was observed that nearly every modification in the method was accompanied by a less thorough removal of the tips and bran layer. Any tips will of course detract from the appearance. This is also true of the incompletely removed bran layer, which gives the grains a "curly" or "fuzzy" coat. Moreover, a complete removal of the bran layer permits the grain to swell better.

A process has finally been developed which will decidedly lower the alkalinity of lye hominy and which should be entirely practicable and easy to apply on a commercial scale. This can be done by a process of scrubbing or abrasion by means of a drum made of No. 12 grater bodies, 9 in. long by 6 in. wide. Twenty of these bodies were soldered together in such a fashion as to form a cylinder 1 ft. long and 7.5 ft. in circumference. Ends for this cylinder were made of tin plate. A narrow sliding door was made to introduce the hominy. This drum was revolved at the rate of 45 r. p. m., in a pan of water of such depth that the hominy slid smoothly down as the drum turned instead of being carried up and dropped down.

A number of brushes were introduced inside this drum, but they only complicated matters and did no apparent good in the apparatus. It is possible that passing the hominy over such a grating surface while it was being shaken would prove more satisfactory. Possibly to some plants a continuous process would be best adapted. In such a case the effect of the length of the lying period must be duly taken into account. When a kettle of hominy is sufficiently lyed it is very essential that its entire contents be emptied at once and the hot lye solution thoroughly rinsed off. A scrubbing process in boiling water may be more effective and is worthy of being tried commercially.

It was found that in this size of drum a 5-min. rotation was about the optimum when 10 lbs. of corn were used. A 12-ft. cylinder would handle 120 lbs. in 5 min. or 600 lbs. in 25 min. The latter figures represent a normal factory batch and an average lying period. Therefore, there should be no practical difficulty in its use from this standpoint.

TABLE VII—EFFECTS OF SCRUBBING PROCESS

No.	43.5 Per cent NaOH Grams	Time of Lying Min.	Time of Scrubbing Min.	pH
1	1050	17	0	7.76
2	1050	17	5	7.26
3	1050	17	10	7.25
4	1050	17	15	7.26
5	1050	24	0	7.84
6	1050	24	5	7.42
7	1050	24	10	7.32
8	1050	24	15	7.22
9	1050	31	0	7.78
10	1050	31	5	7.46
11	1050	31	0	7.38
12	1050	31	15	7.26
13	1600	10	0	7.26
14	1600	10	5	6.92
15	1600	10	10	6.92
16	1600	10	15	6.91
17	1600	15	0	7.75
18	1600	15	5	7.34
19	1600	15	10	7.29
20	1600	15	15	7.23
21	1600	20	0	7.89
22	1600	20	5	7.39
23	1600	20	10	7.37
24	1600	20	15	7.38
25	750	18	0	7.22
26	750	18	5	7.02
27	750	18	10	6.94
28	750	18	15	7.06
29	750	25	0	7.28
30	750	25	5	7.17
31	750	25	10	7.04
32	750	25	15	6.98
33	750	32	0	7.74
34	750	32	5	7.50
35	750	32	10	7.34
36	750	32	15	7.24

There are three very decided advantages in such a procedure. First, it aids in removing the hulls or outer layer of the grains, in which is located the relatively highly alkaline product resulting from the lying process. Second, the usual lying process can be shortened because the mechanical abrasion in part takes the place of the lying process in removing the hulls. In this way it helps further to reduce the alkalinity. Third, by removing this outer hull so effectively it gives a whiter product than can be obtained by any other known process, except by bleaching, and the whiteness is not the dead chalky whiteness obtained by a bleaching process. It is the natural and pleasing whiteness of the corn which is lost in the present methods of hominy making.

Just how efficient a process of scrubbing will be in the prevention of discoloration in hominy cannot be stated without further observations. It will not be effective in all cases, for black has been observed when this process was used. The intensity of the lying process, *i. e.*, the time of lying and strength of the solution, plays a part. When the hominy acquires a high pH due to a severe lye treatment, it can be greatly reduced by abrasion of the grains, but it seems impossible to get it below a certain point, as Table VII will illustrate. It should not be inferred that the H-ion concentration is the only factor which determines the degree of discoloration. The beneficial effect of washing should not be underemphasized. This washing removes to a more or less extent the electrolytes which may have a solvent effect on the iron. Table I gives an example of a hominy with a pH value below the average for commercial hominy, yet the black formation occurred early and was marked. But there was more alkali in it than would be left in a well-washed hominy. In the commercial washing of hominy, the necessity of good stirring should be realized. Since the washing is done in boiling water, a certain amount of hydrogen sulfide is liberated, and less will be formed in the can during processing.

Thirty-six lots of twenty-four No. 2 cans each have been put up in the laboratory from the same corn. In these the time of lying, the strength of the lying solution, and the length of the scrubbing period were all varied to demonstrate the effect on the pH value. Forty pounds of corn were lyed for the time indicated in Table VII, in 80 lbs. of lye solution of the strength noted. It was then rinsed thoroughly, divided into four equal parts, one used as control and the others scrubbed for 5, 10, and 15 min., respectively. Each was then given four 20-min. cooks, and then canned in No. 2 cans, 230 g. per can. The pH was determined a month or more after canning. It should be stated that Nos. 13 to 16, inclusive, and 25 to 36 were all underlyed, not all the tips being removed, even after scrubbing. Half of the cans are stored on end and half on the side. See Table VII.

APPEARANCE AND LOCATION OF BLACK DISCOLORATION

These packs have scarcely been up long enough to justify final conclusions, but it has been noticed that when a can of hominy is allowed to stand on end undisturbed, after processing, there are two ways in which the black ferrous sulfide may show up.

1—A variable amount always forms on the inner surface of the top of the can, notably on the expansion rings and possibly more adjacent to the end seam. So much may form as to flake off, giving the hominy a peppered appearance. It is very similar in appearance to the black which forms in the air space in canned peas and sweet corn. It was evident from these experimental packs that this was formed more abundantly when the hominy was not scrubbed, other conditions being equal.

2—Some grains may become black where they are against the can; at first just a little on a small area, but gradually more until a big portion of the grain is black. In the experimental packs, up to the present time, these grains always lie in a circle adjacent to the bottom seam or against the side seam. In some cases a complete circle has been observed on the bottom. These facts make it appear that the iron for the formation of the black discoloration of hominy comes first from the tin plate where its physical condition has been altered by bending or cutting. If this is true for hominy it seems likely that the iron acquired by other products from the container probably comes first and perhaps largely from these regions.

This clear-cut picture is never met in a commercial can of hominy, as a result of its being handled in transportation and in trading. The first form of black is of little consequence because it is washed off frequently enough and so finely distributed in the can that it is seldom serious. The black grains, however, make it unfit for the trade, not from the standpoint of wholesomeness, but of appearance.

It is not to be concluded that black discoloration would not occur if a can could be made without sharp bends or without the tin plate having undergone some strain. Under such circumstances the formation of black might be retarded but it would be likely to occur within the period of manufacture and consumption of a pack. It is known that the tin on tin plate does not form a complete and continuous coating. Every type of tin container has in it one or both of the conditions of a fractured tin coating, a strain in the plate due to bending or the cut edge of the plate exposed. In the case of the sanitary double seam, the lock side seam, and the expansion rings, the tin coating is more or less broken. In the lap side seam a cut edge of the plate is exposed. This is also true on the end and around the hole of the hole and cap cans.

The Determination of Carbon Dioxide in Self-Rising Flour[1]

By Benjamin R. Jacobs[2]

National Cereal Products Laboratories, Washington, D. C.

The following method of determining carbon dioxide by absorption in barium hydroxide has given very satisfactory results with self-rising flour. Contamination with atmospheric carbon dioxide is avoided by aspirating CO_2-free air through the apparatus, by working rapidly, and by keeping apparatus and reagents properly stoppered. The titration must be carried to a definite end-point.

In consideration of the enormous increase in the production of self-rising flours and of the large number of millers who are manufacturing them practically without chemical control, it seems desirable to present a rapid and accurate method of determining carbon dioxide in this product.

Since the determination of carbon dioxide is made for a large variety of purposes, many methods and many forms of apparatus have been devised. Some require very elaborate apparatus and precautions, and the sources of error are many. Truog[3] determined carbon dioxide in certain soil investigations by the alkali titrimetric method, using measured amounts of barium hydroxide, in which the carbon dioxide was precipitated as barium carbonate which is practically neutral to phenolphthalein. The excess of barium hydroxide was determined by titration and the amount of carbon dioxide by difference.

The Truog method has been adapted by Gurgar[4] to the determination of carbon dioxide in plant respiration studies. The apparatus used by Gurgar is more elaborate than that of Truog, but it is also susceptible of greater accuracy, owing to the use of more dilute reagents, as well as to the precautions used against exposing the standard barium hydroxide solution to the atmosphere.

In determining carbon dioxide in self-rising flours the tendency of the sample to lump when treated with water must be overcome; otherwise small lumps of dough containing dry flour in the center will cause errors in the determination. It has been found that this may be overcome by adding only enough water to form a thick paste, the amount required being about three times the weight of the sample. Vigorous shaking is necessary to break up the lumps and form a homogeneous paste.

Apparatus

The apparatus shown in the accompanying figure consists of a tower, A, a flask, B, of 1000-cc. capacity, a 300-cc. round-bottomed flask, D, provided with a 100-cc. separatory funnel, C, and a glass bulb, E, connected with two 16-oz. bottles, F, filled with 50 per cent sodium hydroxide solution and perforated or solid glass beads, G.

Reagents

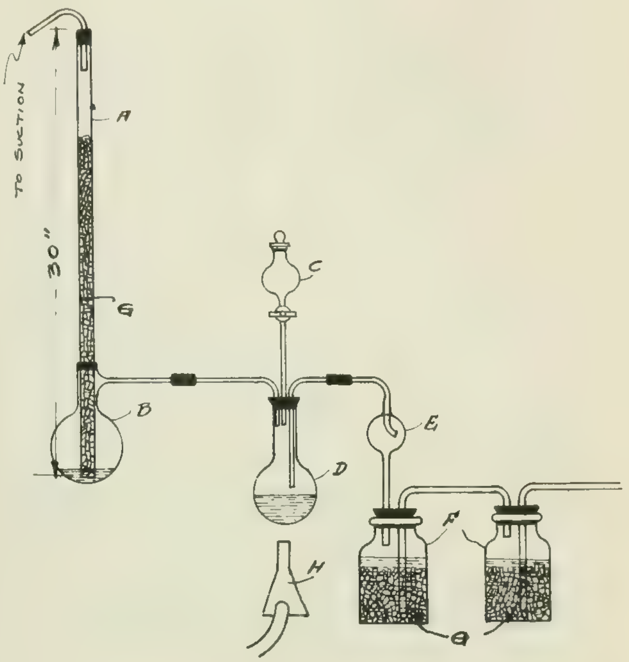
STANDARD HYDROCHLORIC ACID—A 0.1 N solution is used.

BARIUM HYDROXIDE—Seven g. of $Ba(OH)_2$ are dissolved in 1 liter of boiling water and filtered into a stock bottle which has been freed from carbon dioxide. A double filter paper is used and the funnel is never allowed to run dry until the solution has all gone through. Fifty cc. are used for each determination. About 19 cc. of 0.1 N HCl are required to neutralize this amount of barium hydroxide.

PHENOLPHTHALEIN—One gram of phenolphthalein is dissolved in 100 cc. of 95 per cent ethyl alcohol. Four drops are used for each determination.

CO_2-FREE WATER—This may be made either by passing CO_2-free air through water for 30 min. or by boiling for 15 min.

DIASTASE SOLUTION—This is made by dissolving 1 g. of diastase in a liter of CO_2-free water. 100 cc. are used for each determination. This solution should be made up fresh every day.



Procedure

Fifty cc. of the barium hydroxide solution are introduced into flask B through the tower A, the apparatus having previously been freed of CO_2 by drawing CO_2-free air though it for 20 min. Approximately 5 g. of the flour to be tested are weighed in a test tube and dumped into dried flask D, which is immediately corked for future use or connected with the rubber stopper provided with the separatory funnel C. Air is then passed through at the rate of about four bubbles per second. One hundred cc. of the standard diastase solution are run into the separatory funnel. Approximately 15 cc. of this solution are introduced into the flask containing the sample and shaken gently until a homogeneous paste is obtained, whereupon the remaining portion of the diastase solution is introduced. Flask D is immersed in a dish containing water at 70° C. for about 10 min. in order to hasten the action of the diastase on the starch. The temperature of the water in the dish is then increased to boiling, the flask is shaken occasionally, and the determination continued for a total of 25 min. Just before the end of this time a flame is applied directly to the bottom of the flask and the contents are brought to a boil for a few seconds. This should be done carefully to avoid charring.

When the determination is completed the section is closed off with a stopcock connected to the tubing above the tower. The apparatus is disconnected at the side tube of the flask

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[1] Received January 18, 1922.

[2] Director, National Cereal Products Laboratories.

[3] This Journal, **7** (1915), 1045.

[4] *Plant World*, **20**, 288.

B. The tower is raised a few inches, and the beads are allowed to slide out. It is then washed with a little CO_2-free water. The washing is done quickly and if the flask is then corked or the titration made immediately there is scarcely any possibility of contamination from the air. The barium hydroxide solution may be titrated by adding four drops of phenolphthalein indicator. Titrate with hydrochloric acid to the permanent disappearance of the last traces of pink color. If it is desired to determine the residual CO_2 in the sample, flask B and tower A are immediately replaced by another similar flask and tower, which have been previously freed from CO_2 and contain 50 cc. of barium hydroxide solution. Five cc. of concentrated hydrochloric acid are added through the separatory funnel C to the flask containing the sample. The solution is then brought to a boil and the boiling continued very gently, the total time of aspiration being 25 min.

The carbon dioxide obtained from the diastase solution is assumed to be available carbon dioxide, while that obtained from the same solution after the addition of the concentrated hydrochloric acid is assumed to be residual carbon dioxide.

Accuracy of Method

The accuracy of the above method and the efficiency of the apparatus and technic in preventing contamination of the reagents by the carbon dioxide of the air were tested by using measured quantities of standard barium hydroxide in the regular way in the tower and passing CO_2-free air through it for 25 min.

A number of blank determinations were made on commercial grades of flour. In no case was there found to be more than 0.008 per cent of total carbon dioxide, while in several instances the blanks were nil. The method was also tried by using ordinary flour containing no added carbon dioxide and adding known quantities of baking powder of known composition. The baking powder used was a sample which has been used in collaborative work by the Association of Official Agricultural Chemists. It had been tested by five chemists and showed an average of 16 per cent total CO_2. In one instance the sample tested contained 24 mg. of total carbon dioxide and there were recovered 23.60 mg. In another instance the sample analyzed contained 48 mg. of carbon dioxide and there were recovered 46.56 mg.

An Electro-Volumetric Method for Lead[1,2]

By **D. A. MacInnes**[3] and **Eric B. Townsend**

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In the method described in the following paper, lead peroxide, deposited electrolytically, is determined by solution in oxalic acid and titration of the excess acid with potassium permanganate. The method seems more rapid than the usual electro-gravimetric method, and is more accurate, since it involves no uncertain empirical factor. It is unaffected by hydration of the deposit and by all inclusions in the material unless they are oxidizing in nature.

It would also appear that this work establishes, beyond question, the fact that the substance produced by the anodic oxidation is lead peroxide, and contains no higher oxide, as has been claimed by several authors.

In a study of the reactions occurring in the lead accumulator,[4] one of the authors, with his associates, showed that the product of the oxidation of lead at an anode is PbO_2, and not a mixture of this substance with a higher oxide, as has been claimed by Féry[5] and others. However, in the usual electrolytic determination of lead, in which the metal is determined by weighing the dried peroxide, it has been found necessary to use an empirical factor, smaller than the stoichiometrical factor, 0.8663. A low factor may be due to contamination with a higher oxide, or to a persistent hydration of the deposit. For the practical purpose of determining lead, this would not be of importance if there were certainty as to the value of this factor. Hollard,[6] who believes that the discrepancy between the factor for pure PbO_2 and that observed experimentally is due to a higher oxide, obtained values, with a polished anode, varying from 0.740 for small amounts of lead to 0.861 for large amounts. With a roughened electrode he obtained the average value 0.853 for all amounts of oxide, but his experimental deviations were ±0.005 from this factor. Treadwell,[7] on the other hand, recommends a *high* value of the factor, 0.886, for small amounts of oxide, and a lower one, 0.863, for larger quantities. This is far from being a summary of the work on this subject, but it is sufficient to indicate that there is considerable uncertainty as to the value of the factor.

It occurred to the writers that the oxidizing power of the deposited peroxide, on an excess of oxalic acid for instance, could be made the basis for a convenient method of determining lead. Strangely enough, this rather obvious method has received practically no attention. A search through the journals and textbooks disclosed just two references to the method as a possibility and no evidence that it has been tried. Treadwell[8] says, "In a large excess of oxalic acid the lead peroxide (dried at 200°) goes very slowly into solution. The titrimetric determination of the peroxide is, therefore, slow and not to be recommended." Further, Scott[9] suggests such a method, but he states, in a personal communication, that he has not put it to actual test. It was, therefore, considered desirable to try the oxidizing property of the deposited oxide as a means of determining lead.

After some preliminary experiments with a gauze anode, it was found that the best deposits for this purpose were obtained with an anode consisting of a platinum dish, 9 cm. in diameter, roughened on the inside, and a platinum disk, rotating at about 600 r. p. m., as cathode. Small pieces of sheet lead were carefully cleaned and weighed, and dissolved in the anode dish, with 10 cc. of concentrated nitric acid and 15 cc. of water. The sheet lead was kindly furnished by the Bureau of Standards and contained impurities amounting to not more than 0.04 per cent. The resulting solution was electrolyzed with a current of about 12 amp., until the solution gave no test for lead, which was usually after about 30 min. The deposit was then washed with a little distilled water.

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[1] Received January 19, 1922.

[2] Published as Contribution No. 144 from the Research Laboratory of Physical Chemistry, M. I. T.

[3] Associate Professor of Physicochemical Research, M. I. T.

[4] MacInnes, Adler and Joubert, *Trans. Am. Electrochem. Soc.*, **37** (1920), 641.

[5] *Lumière élec.*, **34** (1916), 305; *J. Phys.*, **6** (1916), 21.

[6] *Bull. soc. chim.*, **29** (1903), 151; **31** (1904), 239.

[7] "Electro-analytische Methoden," 148

[8] *Loc. cit.*, 150.

[9] "Standard Methods of Chemical Analysis," 240.

At this point, instead of drying and weighing, the peroxide was determined by one of two methods: (*a*) treatment with potassium iodide and titration of the liberated iodine with sodium thiosulfate, and (*b*) solution in an excess of standard oxalic acid and titration with potassium permanganate of the excess oxalic acid remaining after the reaction. These procedures will be discussed separately.

THE IODOMETRIC METHOD

The procedure followed was that described by Treadwell and Hall[10] for determining lead peroxide. About 0.6 g. of potassium iodide and small amounts of acetic acid and sodium acetate, dissolved in 25 cc. of water, were placed in the anode dish before the deposit had been allowed to dry. It was found, however, that the deposit dissolved very slowly and then only by constant rubbing with a glass rod. From 1.5 to 2 hrs. were necessary for the solution. Heating of the mixture to hasten solution was not advisable because iodine would undoubtedly vaporize to a certain extent. The liberated iodine was titrated with sodium thiosulfate which had been standardized in the usual manner against the potassium permanganate solution described below. Some results of this procedure are given in Table I.

TABLE I—IODOMETRIC DETERMINATION

	Time of Deposition Min.	Current Amp.	Wt. of Lead Grams	Wt. of Lead Determined Grams	Error Per cent
Expt. 1	32	12.4	0.0846	0.0843	−0.4
Expt. 2	40	13	0.2004	0.2000	−0.2

The low results are undoubtedly largely due to the difficulty of getting the deposit completely into solution in the mixture used. This procedure does not seem to be adapted to practical use.

THE OXALIC ACID METHOD

An excess of standard oxalic acid (about 25 cc. of 0.1 *N*) together with 5 cc. of concentrated nitric acid were placed on the peroxide deposit before it had been allowed to dry. The solution was heated to about 80°, until the solid had completely dissolved, which took about 5 min. It is important to keep the volume of the solution as small as possible, as the accuracy of the permanganate titration is greater when using concentrated solutions. After the solution had been transferred to a small beaker and a small amount of concentrated sulfuric acid had been added to precipitate the lead, the excess of oxalic acid was titrated with permanganate solution which had been standardized against pure dry sodium oxalate. The burets and weights used had been carefully calibrated. Some results obtained by this method are outlined in Table II.

TABLE II—OXALIC ACID METHOD

EXPT.	Current Amp.	Time of Deposition Min.	Weight of Lead Taken Grams	Weight of Lead Found Grams	Error Per cent
1	13.0	45	0.0889	0.0888	−0.11
2	13.0	40	0.0906	0.0904	−0.22
3	12.0	35	0.1604	0.1606	+0.12
4	12.2	30	0.1793	0.1792	−0.06
5	11.8	32	0.1772	0.1773	+0.06
6	12.6	30	0.1867	0.1868	+0.05
7	11.0	41	0.2113	0.2115	+0.10
8	12.2	30	0.1939	0.1938	−0.05

This combined electrolytic and volumetric method appears to be more rapid than the usual electro-gravimetric determination, and is certainly more accurate, since it involves no uncertain empirical factor. There does not seem to be any observable difference in accuracy when large and small amounts of lead peroxide are deposited, which indicates that the variation in the empirical factor considered above is probably due to differences in hydration rather than to variation in the chemical nature of the deposit. The determination is unaffected by hydration of the deposit, and by all inclusions in that material, unless they are oxidizing in nature. It has, of course, all of the advantages of the electrolytic method. "By this (electrolytic) method the lead is separated from zinc, cobalt, nickel, iron, aluminium, cppper, gold, mercury, antimony, and cadmium. Traces of silver and bismuth, if present, are deposited as peroxides with the lead."[11]

Further, this work is in accord with the results of the experiments on the lead accumulator, referred to above. It appears to establish definitely the fact that the product of the anodic oxidation of lead is lead peroxide, which contains no higher oxides.

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[10] "Quantitative Analysis," 675.

[11] Olsen, "Quantitative Chemical Analysis," 222.

The Metric System

So much has been said against the adoption of the metric system that it appears desirable to advance some arguments in favor of its adoption. The following statements are, therefore, quoted from a "Summary of Arguments in Favor of Further Adoption of Metric System," which was prepared by the special committee appointed by the Chamber of Commerce of the United States to consider the metric system.

> 1—The metric system of weights and measures is now firmly established as an international system, either through its legal adoption, or its exclusive or permissive use for standards, by the principal nations of the world. Its more general use in the United States is therefore advocated to promote greater international uniformity, and in the hope, if that be accomplished, that other English-speaking peoples would follow the lead of this country.
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> 2—The system has been proved to be satisfactory in the United States and elsewhere in its use in complicated scientific calculations; and, in the metric countries, adaptable to the everyday trade, and to industrial and educational requirements of the people.
>
> 3—While the basis for the units of the metric system is, of course, arbitrary, it has now been definitely established, and the various decimal gradations give a wide choice for convenient designated measurements of length, weight and capacity, adaptable to common and scientific use. Familiarity with such terms as the pound and inch is largely a matter of habit, and it is believed that habit would also make the use even of the decimal subdivisions of the metric system, such as the millimeter, equally familiar and convenient.
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> 4—The basic simplicity of the system, with its few units, as the meter, liter, gram, with decimal subdivisions, makes both teaching and learning easy; and, in trade, makes billing and computation simple. During the period of transition, when there would for a time be more active dual relations than at present, conversion would be almost automatic through the use of tables of equivalents.
>
> 5—An arbitrary imposition of any system of weights and measures, without a reasonable period of transition or the principle of exemption, where desirable for manufacture or for export to nonmetric countries, might be a hardship. A gradual change has been effected in most metric countries, and it is believed that such change was accomplished without hardship and without such heavy expense as claimed by those opposed to its adoption. It is also believed that greater conformity to the habits of metric countries would tend to increase our export trade. The question of countervailing imports of manufactured goods and raw material is an economic subject quite apart from the question at issue.
>
> 6—The relative international popularity of the two major systems in use is shown by the number of nations which in recent years have adopted the metric system, while none has formally adopted the British-American system, although in population the two groups are about equal. [Since 1914, Poland, Latvia, Russia, Japan, Haiti, and Esthonia have become metric.]

A pamphlet entitled "Uehling CO_2 Equipment" has been prepared by the Uehling Instrument Company for guiding the engineer and fireman in reducing the waste of fuel up the chimney.

The Determination of Bromide in Brines and Mineral Waters[1]

By C. C. Meloche[2] and H. H. Willard[3]

Chemical Laboratory, University of Michigan, Ann Arbor, Michigan

A detailed study has been made of the various factors affecting the separation of bromine from very large amounts of chloride by oxidation with excess of permanganate and a carefully regulated amount of hydrochloric acid. The bromine containing a little chlorine after absorption in alkali is reduced and precipitated with silver. The mixed silver halides are fused in chlorine and from the loss in weight the amount of bromine is calculated.

If iodide is present it is first oxidized to iodate by permanganate in alkaline solution, after which the bromine is distilled off as usual. The iodate remaining may be determined by titration with thiosulfate.

The method as finally recommended is accurate and more rapid than other methods of equal accuracy. It is suitable for brines and similar substances and very large samples can be used.

The accurate quantitative determination of small amounts of bromide in the presence of large amounts of chloride has always been a matter of considerable difficulty. Most of the methods hitherto suggested seek, by regulation of the acidity or choice of the oxidizing agent or both, to arrange conditions so that the bromine can be liberated and distilled off while the chlorine remains in the residue as chloride. A satisfactory separation is possible when the concentration of chloride is low, but high concentration of chloride renders the quantitative separation of small amounts of bromine in one operation almost impossible. For this reason, it is advisable to carry out a preliminary concentration process with a strong oxidizing agent and a strong acid, making certain that the bromine is entirely recovered along with some chlorine. The bromine in the distillate can then be determined with precision.

The method recommended is briefly as follows: The sample of brine, somewhat diluted if necessary, is treated with an excess of permanganate and hydrochloric acid, heated, and the bromine removed by means of a current of air. The bromine, together with some chlorine, is absorbed in sodium hydroxide solution, reduced to bromide and chloride, preferably by hydrazine sulfate, acidified with nitric acid, and precipitated by means of silver nitrate. The weight of bromine is calculated from the loss in weight of the mixed silver halides on ignition in chlorine.

A bibliography on the determination of bromine is given by Baughman and Skinner.[4] The work of Baubigny[5] is of particular importance in the present case.

Apparatus and Reagents

The apparatus used in this investigation (Fig. 1) consisted essentially of a 250-cc. steam-jacketed retort, A, a 10-bulb tube, B, a saturator, C, a flowmeter, D, a pressure regulator, E, and a source of pure compressed air.

The retort was provided with the air inlet tube, *a*, which was ground to fit and extended nearly to the bottom. The tubulus was bent at an angle of about 80° as shown. The slip joint between the tubulus and the 10-bulb tube was rendered gastight by means of a short piece of rubber tubing.

The air current before entering the retort passed through a soda-lime tower, not shown, through the regulator, the flowmeter, and the saturator. The regulator consisted of a long tube, *b*, connected with the main air line and dipping in water contained in a tall cylinder. By means of the screw pinchcock *c* the air supply was so regulated that a little was continually escaping through *b*. By adjusting the level of water in the cylinder the pressure could be fixed as desired, and in this way the rate of passage of the air could be maintained at any definite value up to 80 l. per hr. For high rates, the water in the cylinder was partly replaced by mercury. The rate of passage of the air was indicated by the flowmeter.

The saturator was a steam-jacketed, 250-cc. distillation flask containing 2 g. of sodium hydroxide dissolved in about 150 cc. of water. The inlet tube extended nearly to the bottom of the flask.

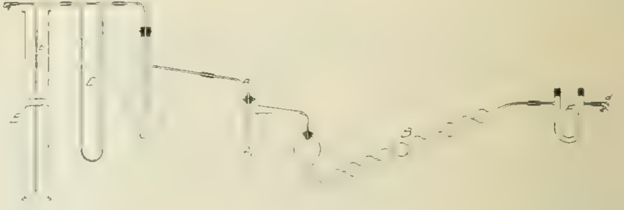

Fig. 1

The 10-bulb tube was of ordinary dimensions, each bulb being about 30 mm. in diameter and the constricted portions about 6.5 mm. in diameter.

The guard tube F, containing very dilute silver nitrate solution, a little hydrazine sulfate, and a few drops nitric acid, served to detect any loss of halogen.

The standard bromide solution was made by dissolving in distilled water specially purified potassium bromide.[6] The strength of the solution was determined by precipitation and weighing of fused silver bromide and also by determination of the loss in weight of the silver bromide on ignition in chlorine. The results obtained by the two methods were in close agreement, thus proving the absence of appreciable amounts of chloride. The weight of bromine per gram of solution was 0.015787 gram.

The sodium chloride which was added in large amounts was Kahlbaum's best grade. The other materials used were of chemically pure grade. When traces of bromide were present they were determined by blank analyses.

Procedure

In the experiments listed in Tables I to VIII the retort was charged with known weights of standard potassium bromide solution and of sodium chloride, the weighed excess of potassium permanganate was introduced, the solution diluted, and the hydrochloric acid added last, the total volume being 150 cc. for all experiments. The air inlet tube was immediately inserted and the retort connected with the 10-bulb tube which contained 2 g. of sodium hydroxide dissolved in 70 cc. or more of water. After the entire apparatus was connected the air was turned on, and any slight adjustment in rate quickly made. The steam was then turned on under the saturator and under the retort, and the time noted. When the operation had continued the desired length of time, the air

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[1] Received September 15, 1921.

[2] Assistant Professor of Analytical Chemistry, University of Michigan.

[3] Associate Professor of Analytical Chemistry, University of Michigan.

[4] This Journal, **11** (1919), 954.

[5] *Compt. rend.*, **125** (1897), 527; **128** (1899), 1160, 1236.

[6] Prepared by Dr. R. K. McAlpine for use in atomic weight work.

stream was interrupted most satisfactorily by means of a screw pinchcock at *d*. The steam and air supply were then turned off.

After the 10-bulb tube had been disconnected the hypobromite solution containing some hypochlorite was transferred to a 500-cc. glass-stoppered Erlenmeyer flask and reduced by adding a weighed excess of hydrazine sulfate and swirling the flask. The solution was then made approximately 0.2 *N* with nitric acid and the silver bromide, together with some silver chloride, precipitated and washed in the manner usually prescribed for careful work. The precipitate contained in a Gooch crucible supplied with a Rose cover, preferably of quartz, was first thoroughly dried at about 180°, then raised to a temperature somewhat above the fusion point for about 0.5 hr. After cooling and weighing, the precipitate was heated at the latter temperature in a current of chlorine for about 1 hr. with occasional tilting of the crucible. After cooling and weighing again, the operation was repeated, but usually without a noticeable loss in weight. It was found that when fine asbestos of high grade was used and excessive temperatures avoided, very satisfactory results could be obtained without transfer of the precipitate. In heating the Gooch crucibles to the higher temperature, an outer protecting dish was always provided. The amount of bromine was calculated from the loss in weight on ignition in chlorine by use of the factor 1.7976.

After preliminary determination of the approximate conditions necessary, the effect of each of the following factors was studied separately: (1) Duration of passage of air; (2) rate of passage of air; (3) concentration of permanganate; (4) concentration of hydrochloric acid; (5) the amount of chlorine carried over; (6) the concentration of sodium chloride; (7) the concentration of bromide; (8) the presence of iodide; (9) the character of the reducing agent; (10) the presence of other constituents of brine.

DURATION OF PASSAGE OF AIR

Experiments in which the duration of the passage of air was varied from 1.5 to 3 hrs. were run at a rate of 10 l. per hr. The results given in Table I show that when the rate is as low as 10 l. per hr., the recovery of bromine is scarcely quantitative in 3 hrs. It was later demonstrated (Table III) that the bromine could be entirely recovered in 30 min. if the rate of passage of the air was sufficiently increased.

TABLE I—EFFECT OF VARIATION IN DURATION OF PASSAGE OF AIR

Rate = 10 l. per hr.
NaCl present = 25.0 g.; $KMnO_4$ added = 1.0 g.; HCl added[1] = 0.40 g.; total volume of solution in retort, including reagents = 150 cc.

Duration of Passage of Air Hours	Bromine Present Grams	Bromine Found Grams	Error Grams
1.5	0.2586	0.2549	−0.0037
2.0	0.2609	0.2589	−0.0020
3.0	0.2586	0.2580	−0.0006

[1] This means actual HCl, although it was added in the form of a dilute solution.

RATE OF PASSAGE OF AIR

The effect of increasing the rate of passage of the air is illustrated by the experimental results given in Table II. At the higher rates, the recovery is more nearly complete in a given length of time. With 10-bulb tubes of ordinary dimensions the rate can be increased to 80 l. per hr. without appreciable loss of bromine. This fact makes possible the complete recovery of bromine in 30 min., as shown in Table III. At rates above 80 l. the accumulation of liquid in the end bulbs is likely to be so rapid that mechanical loss occurs before the end of the experiment; 70 l. per hr. is a convenient rate for accurate work.

TABLE II—EFFECT OF INCREASE IN RATE OF PASSAGE OF AIR

(Conditions same as given under Table I)

Rate of Passage of Air L. per Hr.	Duration of Passage of Air Min.	Bromine Present Grams	Bromine Found Grams	Error Grams
10	120	0.2609	0.2589	−0.0020
20	120	0.2589	0.2580	−0.0009
30	120	0.2583	0.2576	−0.0007
30	60	0.2583	0.2574	−0.0009
40	60	0.2584	0.2580	−0.0004

TABLE III—EFFICIENCY OF RECOVERY OF BROMINE AT HIGHER RATES OF PASSAGE OF AIR

NaCl present = 25.0 g.; $KMnO_4$ added = 0.5 g.; HCl added = 0.3 g.; total volume of solution in retort, including reagents = 150 cc.

Rate of Passage of Air L. per Hr.	Duration of Passage of Air Min.	Bromine Present Grams	Bromine Found Grams	Error Grams
50	30	0.2594	0.2585	−0.0009
60	30	0.2579	0.2578	−0.0001
70	30	0.2591	0.2590	−0.0001
80	30	0.2588	0.2589	+0.0001

CONCENTRATION OF PERMANGANATE

When bromine is liberated by means of an excess of potassium permanganate in hot, slightly acid solution, the permanganate is reduced for the most part to manganese dioxide. If the theoretical amount or only a slight excess of permanganate is used the recovery of bromine is incomplete, as shown in the last experiment, Table IV. No trouble is experienced, however, when a moderate or even a rather large excess is employed as in the first three experiments. Sufficient permanganate has been added if at the end of the distillation the liquid in the retort still retains a deep purple color. For amounts of bromine up to 0.26 g., 0.5 g. of potassium permanganate is recommended.

TABLE IV—EFFECT OF CHANGE OF CONCENTRATION OF POTASSIUM PERMANGANATE

Rate of passage of air = 40 l. per hr.; duration of passage of air = 1.0 hr. NaCl present = 25.0 g.; HCl present = 0.4 g.; total volume of solution in retort, including reagents = 150 cc.

$KMnO_4$ Added Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
5.0	0.2585	0.2583	−0.0002
1.0	0.2584	0.2580	−0.0004
0.5[1]	0.2581	0.2580	−0.0001
0.2[2]	0.2578	0.2565	−0.0013

[1] Permanganate almost entirely reduced.
[2] Permanganate entirely reduced.

CONCENTRATION OF ACID

Increase in the concentration of hydrogen ion favors the liberation of bromine but at the same time favors the liberation of chlorine. The concentration of acid must therefore be carefully regulated if an exact separation is being attempted. Under these conditions, however, there is danger that the bromine may not be entirely recovered. The authors have therefore used a strong acid, as hydrochloric acid, in such amounts that a little chlorine is liberated along with the bromine. The recovery of all the bromine is insured and the small amount of chlorine carried over does no harm. Upon examination of Table V, it will be observed that when a moderate excess of acid is used the results are very satisfactory but when a slight excess only is employed as in the fourth experiment, the results are far from quantitative. From 0.3 to 0.4 g. of actual hydrochloric acid is recommended when the amount of bromine present does not exceed 0.26 g.

TABLE V—EFFECT OF CHANGE IN CONCENTRATION OF HYDROCHLORIC ACID

Rate of passage of air = 40 l. per hr., duration of passage of air = 1 hr. NaCl added = 25.0 g.; $KMnO_4$ added = 0.5 g.

HCl Added Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
0.4	0.2594	0.2592	−0.0002
0.3	0.2587	0.2588	+0.0001
0.2	0.2589	0.2585	−0.0004
0.16	0.2589	0.2508	−0.0081

Chlorine in Distillate

The amount of chlorine carried over in the course of removal of the bromine increases with increase in concentration of hydrogen ion and of the oxidizing agent. When these factors remain constant, the amount of chlorine carried over decreases with increase in the concentration of bromide, as shown by the first three experiments in Table VI. Even the maximum amount, which in any case does not much exceed 0.2 g., exerts no harmful effect. The only additional information needed for the determination of chlorine in the distillate is the weight of the empty crucible, which is not ordinarily obtained if bromine alone is required. The chlorine derived from the sodium hydroxide should of course be subtracted. In each experiment given the recovery of bromine was quantitative, as shown in Table VIII.

Table VI—Weight of Chlorine in Distillate as Affected by Concentration of Bromide

Rate of passage of air = 70 l. per hr.; duration of passage of air = 30 min., except in last experiment, where it was 45 min.

NaCl present = 25.0 g.; total volume of solution, including reagents = 150 cc.

HCl Added Grams	$KMnO_4$ Added Grams	Bromine Present Grams	Chlorine in Distillate Grams
0.3	0.5	0.0000	0.2082[1]
0.3	0.5	0.0108	0.1457
0.3	0.5	0.0522	0.1020
0.6	1.0	0.5154	0.2145
0.6	1.0	0.5148	0.2138

[1] Average of two determinations.

Concentration of Sodium Chloride

The presence of large amounts of sodium chloride retards very noticeably the separation of bromine. Conditions which are satisfactory for the quantitative recovery of bromine when other salts are present in low concentration may prove entirely inadequate when the concentration of other substances is high. Having observed this fact in preliminary work, practically all experiments have been conducted with sodium chloride present in high concentration in order that the conclusions reached may be safely applied to brine analysis. The retardation of the evolution of bromine when a high concentration of sodium chloride exists is due probably to the formation of perhalide and to the lowering of the vapor tension. The results given in Table VII show the amount of discrepancy observed. Low results had previously been obtained in the case of Expt. 1 because of insufficient permanganate, in the case of Expt. 3 because of insufficient acid, and in the case of Expt. 5 because of the low rate of passage of air, but in every case the repetition of the experiment with 1.0 g. instead of 25.0 g. sodium chloride showed a material improvement in the recovery of bromine.

Table VII—Effect of High Concentration of Sodium Chloride

Total volume of solution, including reagents = 150 cc.

Expt.	$KMnO_4$ Added Grams	HCl Added Grams	Duration of Passage of Air Hrs.	Rate of Passage of Air L. per Hr.	NaCl Present Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
1	0.2	0.4	1.0	40	25	0.2578	0.2565	−0.0013
2	0.2	0.4	1.0	40	1	0.2576	0.2572	−0.0004
3	0.5	0.16	1.0	40	25	0.2589	0.2508	−0.0081
4	0.5	0.16	1.0	40	1	0.2601	0.2538	−0.0063
5	1.0	0.4	2.0	10	25	0.2609	0.2589	−0.0020
6	1.0	0.4	2.0	10	1	0.2603	0.2593	−0.0010

Concentration of Bromide

Since the bromine content of brines and bitterns may vary considerably, it is important that the method used should have a wide range of application. The results given in Table VIII were obtained with amounts of bromine varying from 0.01 to 0.50 g. The conditions were chosen so as to duplicate as nearly as possible those recommended by the authors for an actual brine analysis. It will be noted that the errors are small and the method very accurate. It is more convenient to work with samples containing 0.25 g. of bromine or less, but a larger amount of bromine, *e. g.*, 0.5 g., may be present, providing the requisite excess of hydrochloric acid and of potassium permanganate is added and the ignition in chlorine continued somewhat longer.

Table VIII—Effect of Varying Concentration of Bromide

Rate of passage of air = 70 l. per hr.; duration of passage of air = 30 min., except in last experiment, which was run for 45 min.; NaCl present = 25.0 g.

HCl Added Grams	$KMnO_4$ Added Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
0.3	0.5	0.0000	0.0003	+0.0003
0.3	0.5	0.0108	0.0108	0.0000
0.3	0.5	0.0522	0.0521	−0.0001
0.3	0.5	0.2591	0.2590	−0.0001
0.6	1.0	0.5154	0.5157	+0.0003
0.6	1.0	0.5148	0.5150	+0.0002

Presence of Iodide

The amount of iodide present in a natural brine is often so small that it may be disregarded, especially if the permanganate is added first to the neutral solution and the acid added last. If desired, the iodine can be distilled over with the bromine. In this case the acid is added first and the permanganate last, to avoid oxidation to iodate. The iodine is then determined in a separate sample and the proper correction applied to the loss in weight on ignition in chlorine before the bromine is calculated. When significant amounts of iodide are present the bromine may be directly determined and the necessity for the determination of iodine avoided by the following modification:

The sample of brine is made distinctly alkaline, treated with an excess of permanganate, and boiled to convert iodide to iodate. After cooling, the customary excess of acid is added and the determination finished as usual. If an excess of permanganate is present during the entire operation the iodine remains in the form of iodate and the interference of iodide is effectively eliminated, as the results in Table IX show.

Table IX—Effect of Presence of Iodide on Determination of Bromine

Rate of passage of air = 70 l. per hr.; duration of passage of air = 30 min.

NaCl present = 20.0 g.; wts. $KMnO_4$ and HCl calculated as explained above.

Iodine Present Grams	Iodine Found Grams	Error Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
0.0659	0.0655	−0.0004	0.2582	0.2585	+0.0003
0.1243	0.1250	+0.0007	0.2572	0.2575	+0.0003

The experiments there given were conducted as follows: The neutral solution containing bromide, iodide, and a large excess of chloride was treated with sufficient sodium hydroxide (about 0.1 g.) so that the green color of the manganate developed when the permanganate was added in the cold. The amount of potassium permanganate added was slightly more than the weight calculated to oxidize iodide to iodate plus the usual 0.5 g. for the liberation of bromine. After boiling for 2 min. the solution was cooled and an amount of hydrochloric acid, slightly more than sufficient to neutralize the added alkali and the alkali formed on reduction of the permanganate by iodide, was introduced, in addition to the 0.3 g. of hydrochloric acid usually used. After diluting to 150 cc. the bromine was removed by a current of air in the usual way.

The residue in the retort was used for the determination of iodine by the method of Baughman and Skinner,[7] modified as follows: The solution after dilution was treated with sufficient sodium peroxide to reduce the permanganate, boiled for 10 min. or more to remove any excess of peroxide, and filtered from the precipitate of manganese dioxide. The iodine which remained in the form of iodate was determined by adding the neutralized solution to an excess of potassium iodide solution containing hydrochloric acid. The liberated iodine was titrated with standard sodium thiosulfate in the usual manner. Since six atoms of iodine are liberated for every atom of iodine originally present, the method is well adapted for the determination of small amounts of iodine.

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[7] This Journal, 11 (1919), 563.

Reducing Agent

The quantitative absorption of bromine vapor from its mixture with air by means of dilute alkali presents no difficulties whatever, as shown in discussing the rate of passage of air. The resulting solution, however, contains hypobromite and hypochlorite which must be reduced before the ordinary gravimetric method can be applied. In the experiments previously described reduction has been accomplished by means of hydrazine sulfate. This reagent is ideal in almost every respect. It reduces hypobromite, hypochlorite, bromate, and chlorate almost instantaneously in the cold. The excess is without reducing action on silver nitrate or dilute nitric acid and therefore need not be removed. It is easily purified by recrystallization. The substance is, however, somewhat expensive and not always obtainable.

Of the more common reducing agents, sodium peroxide and possibly ammonium hydroxide are preferable to sulfurous acid which is sometimes used. Boiling is required in both instances and the solution must be cooled again before nitric acid can be added. Neither of the reagents is effective for the reduction of bromates and chlorates, should these be present. The results given in Table X were obtained when these reagents were substituted for the hydrazine sulfate. For the first experiment 2.0 g. of sodium peroxide were slowly hydrated, then added to the hypobromite-hypochlorite mixture and the alkaline solution boiled for 15 min. In the second experiment an excess of ammonium hydroxide was added and the solution boiled for 5 min.

Table X—Efficiency of Other Reagents for Reduction of Hypobromite

(Conditions otherwise the same as for first four experiments, Table VIII)

Reagent	Bromine Present Grams	Bromine Found Grams	Error Grams
Na_2O_2	0.2577	0.2577	0.0000
NH_4OH	0.2581	0.2574	−0.0007

Effect of Other Constituents of Brine

To learn the effect of other constituents of brine, synthetic brines were prepared containing large amounts of sodium chloride, calcium chloride, and magnesium chloride together with a small amount of ferric chloride and a carefully determined weight of potassium bromide. During analysis the rate of evolution of chlorine and bromine was noticeably increased, as a result of the catalytic effect of ferric chloride. To avoid a slight loss at the beginning of the operation, the saturator was not heated for the first 5 or 10 min. The determination of bromine gave very satisfactory results, as shown in Table XI.

Table XI—Determination of Bromine in Synthetic Brine

Other constituents: $NaCl$ = 20.0 g.; anhyd. $CaCl_2$ = 2.5 g.; anhyd. $MgCl_2$ = 2.5 g.; anhyd. $FeCl_3$ = 0.048 g.; other conditions same as for first four experiments, Table VIII

Bromine Present Grams	Bromine Found Grams	Error Grams
0.2573	0.2568	−0.0005
0.2101	0.2098	−0.0003

The presence of considerable calcium and magnesium is ordinarily without marked effect, as the experimental results show, but when significant amounts of iodide are also present and it is desired to use the modification previously described, complications are introduced. When the solution is made alkaline preparatory to the oxidation of iodide to iodate, the mixed precipitate of magnesium hydroxide, calcium hydroxide, and calcium carbonate obtained is inconveniently bulky. If sufficient alkali is added to precipitate only part of the magnesium, loss of bromine is likely to occur on boiling. Under these conditions it is advisable to remove the iron, calcium, and magnesium as explained below.

Determination of Bromine in Natural and Artificial Brines

PROCEDURE IN ABSENCE OF IODIDES—A sample of brine containing not more than 0.3 to 0.5 g. of combined bromine, and in any case not more than 100.0 g. of concentrated brine, is transferred to the retort. According to the amount of bromine present, 0.5 to 1.0 g. of potassium permanganate is added in the cold. Before adding the acid the 10-bulb tube is charged with a solution containing 2.0 g. of sodium hydroxide "from sodium" in 80 cc. of water and the apparatus is otherwise placed in readiness. Hydrochloric acid (best in the form of a dilute solution) is added to the brine in sufficient amount to provide 0.3 to 0.6 g. of free HCl, depending on the amount of bromine present. After dilution to 150 cc., the apparatus is immediately connected up and the analysis finished as already described.

PROCEDURE WHEN IODIDES ARE PRESENT—A sample of brine containing at the most 0.5 g. of combined bromine, 0.2 g. of combined iodine, and such amounts of iron, calcium, and magnesium that the removal of these elements can be conveniently accomplished, is diluted and treated hot with an excess of sodium hydroxide and sodium carbonate. After filtration and washing the filtrate is neutralized, concentrated to 100 cc., made alkaline to the extent of 0.1 g. of free sodium hydroxide, and transferred to the retort. A slight excess of potassium permanganate above that required to oxidize iodide to iodate plus the usual 0.5 to 1.0 g. is added in the cold without stirring. If the green color of manganate develops, conditions are satisfactory for the complete oxidation of iodide to iodate. If the green color does not appear, either the concentration of iodide is very low or insufficient alkali has been added. The odor of halogen indicates that insufficient alkali is present. The solution is boiled for 2 min., noting the odor at first to make sure that no halogen is lost, then cooled. Sufficient hydrochloric acid is added to provide the usual 0.3 to 0.6 g. of free HCl and the analysis finished as above directed. As much as 100 g. of strong brine may be used as a sample, providing the conditions as first stated are complied with. If desired, the residue in the retort may be used for the determination of iodine as previously described.

Determination of Bromine in Mineral Waters

A sufficiently large volume of the mineral water should be evaporated to give a total bromine content of several milligrams, if possible. Larger volumes may be evaporated if greater accuracy is desired. The concentrated solution or the residue taken up with a little hydrochloric acid is then analyzed for bromine by the method above described for brines.

The Council of the Optical Society of America has decided to hold an optical instrument exhibit during the annual meeting of the Society at the Bureau of Standards, Washington, D. C., next October. To enable the exhibit committee to plan the space adequately and assign it equitably, it requests those interested to submit the following information: What instruments are offered for exhibition? How much floor space would be necessary? What additional facilities other than space will be needed? When the information is at hand the exhibit committee will notify the prospective exhibitors of the amount of space allotted to them, and will see that the general laboratory facilities necessary are provided. The exhibitors will instal their own exhibits and meet the expenses incident thereto.

Notes on the Analysis of Cast Bronze[1,2]

By **G. E. F. Lundell** and **J. A. Scherrer**

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Many of the observations which are noted in the following pages are known, but they merit repetition because they represent desirable procedures and precautions which are often ignored. The method of analysis which is given is based on work done at the Bureau of Standards and by the coöperating analysts. It embodies nothing that is new, but possesses merit in that it groups desirable procedures and takes into account the known sources of error.

MOST of the observations contained in this paper were made in connection with the analysis of the Bureau of Standards standard sample of Cast Bronze No. 52. This bronze was chill-cast in 1 in. × 12 in. × 24 in. slabs under the supervision of Mr. P. E. McKinney at the Naval Gun Factory, Washington, D. C., and subsequently machined and mixed at the Bureau. Preliminary analyses demonstrated that the mixed sample was remarkably uniform in composition and that it was free from arsenic and phosphorus. The general composition of the bronze was fixed by the Advisory Committee on Nonferrous Metals and the actual composition as determined at the Bureau and by the coöperating analysts is as follows: copper, 88.33; tin, 7.90; zinc, 1.89; lead, 1.52; antimony, 0.16; nickel, 0.13; and iron, 0.12. The following firms coöperated with the Bureau of Standards in its analysis:

The American Brass Co.
Bridgeport Brass Co.
Scovill Manufacturing Co.
The Ajax Metal Co.
National Lead Co.
Lumen Bearing Co.
Lunkenheimer Co.
The National Cash Register Co.
Crane Company
Ledoux and Co.
A. D. Little, Inc.
Pennsylvania Railroad System
C. B. & Q. Railroad Co.
Naval Gun Factory, Washington, D. C.

Notes on the Methods of Analysis

SEPARATION OF TIN AND ANTIMONY BY DIGESTION WITH NITRIC ACID—In this universally employed separation, the following observations are worthy of note:

(1) Hot digestion of the nitric acid solution of the alloy for 3 to 6 hrs. is desirable and it is imperative to keep the solution and the washing solution *boiling hot* throughout the filtering operation

(2) Evaporation of the nitric acid solution to dryness followed by drenching and digestion with nitric acid is not necessary with alloys containing only tin or ten times as much tin as antimony. The operation does no harm, however, and is desirable with alloys of high antimony content, although in this case complete deposition of antimony is impossible.

(3) Other elements like phosphorus, arsenic and vanadium are quantitatively carried down with tin, provided the ratio of tin to these elements is high enough; in addition, the tin precipitate always carries down more or less of such other alloy constituents as iron, copper, zinc, and silicon.

(4) The complete separation of tin and antimony is often a matter of doubt, owing to such factors as the presence of considerable iron (over 0.25 per cent), the presence of considerable antimony, too short a digestion period, or the acceptance of a filtrate which is not crystal-clear.

DETERMINATION OF COPPER—(1) Equally good determinations are obtained by slow electrolysis and by rapid electrolysis in a solenoid apparatus or with rotating cathodes.

(2) Traces of copper (0.1 to 0.3 mg.) escape deposition in carefully conducted electrolyses and no advantage is ordinarily gained by redeposition. In fact a mechanical loss may result, if the first deposit is dissolved without using proper precautions.

(3) If tin or antimony in the ionic state is present in the electrolyte, it will be deposited to some extent with the copper and consequently the deposit should be examined for these elements.

DETERMINATION OF TIN—(1) Gravimetric determinations of tin as oxide average higher than determinations by other methods and require correction for antimony (and such other elements as phosphorus and arsenic) as separately determined, and for such contaminants as iron, copper, zinc, and silicon as obtained either by actual determination and deduction or by separation and reprecipitation of the tin and antimony.

(2) Stannic oxide and antimony tetroxide are very easily reduced and consequently all reducing gases must be very carefully excluded during the ignition, which is best performed in a porcelain crucible set in a hole in an asbestos shield. When so protected the oxides will stand the full blast.

(3) Ignited tin and antimony oxides can be conveniently put in solution by fusion in a platinum crucible (with occasional stirring with a short platinum rod) with fused borax followed by digestion of the cooled melt in warm, dilute hydrochloric acid. The solution can then be tested for impurities by treating the solution with an excess of potassium hydroxide and hydrogen sulfide.

(4) The electrolytic method affords erratic values, sometimes low, owing perhaps to the lack of a suitable test for complete deposition, and sometimes high, owing to inclusions; this latter effect is often corrected by "blank" electrolyses.

(5) The iodometric method yields excellent results, provided the iodine solution is standardized under like conditions against material of known tin content; the tin titer so obtained is higher than the theoretical. The method is also remarkably free from interfering factors, the ordinary alloy constituents, as well as antimony and arsenic, being without effect.

DETERMINATION OF ANTIMONY—(1) Gravimetric determinations of antimony as Sb_2O_4 or Sb_2S_3 tend to give high values, owing in part to the difficulty in completely removing contaminating impurities. As noted under the determination of tin, Sb_2O_4 is very easily reduced; Sb_2S_3 cannot be satisfactorily ignited in paper.

(2) An accurate and desirable method is the modified Low procedure (oxidation of antimony from the trivalent to the quinquevalent condition by permanganate in cold hydrochloric-sulfuric acid solution). The titer of the permanganate solution obtained by titration against a compound of known antimony content is higher than that obtained by calculation from the iron value. The only interfering substance encountered in ordinary materials is arsenic. Fortunately this is usually absent or present in such small amount that a satisfactory correction can be calculated from the amount present.

DETERMINATION OF LEAD—(1) The electrolytic method yields accurate results when but small amounts of lead are involved and when the electrolyte is free from such interfering substances as manganese and colloidal metastannic acid.

(2) The sulfate method is to be preferred when large amounts of lead are involved or when the electrolyte contains manganese or tin.

(3) There is no apparent advantage in precipitating lead as sulfate and then dissolving it in ammoniun acetate and reprecipitating as chromate or molybdate.

DETERMINATION OF ZINC—(1) Equally good results are obtained by the precipitation of ZnS from formic acid or 0.01 *N* sulfuric acid solutions.

(2) The precipitation of zinc sulfide or phosphate is incomplete in the presence of glyoxime reagent.

(3) The precipitation of zinc as phosphate must be made with diammonium phosphate in very weak acetic acid solution, and the solution must be kept warm until the phosphate becomes crystalline.

(4) The conversion of zinc sulfide to sulfate requires care in order to drive off excess sulfuric acid without loss of sulfur trioxide from the sulfate.

(5) The ignition of zinc sulfide to zinc oxide must be carried out at a low initial temperature until carbon is destroyed, lest there be a reduction and volatilization of zinc; a final temperature of 850° C. is required to convert completely to oxide the sulfate which is formed, and a temperature above 950° C. must be avoided on account of the volatility of zinc oxide.

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[1] Received February 3, 1922.

[2] Published by permission of the Director of the Bureau of Standards.

DETERMINATION OF IRON—(1) The greatest source of error lies in ignoring the iron which is always carried down by tin and antimony during a nitric acid attack; frequently all of the iron is carried down.

(2) In gravimetric determinations corrections should be applied for silica and the possibility of the presence of such elements as aluminium borne in mind.

(3) In volumetric work corrections as indicated in blank determinations should be applied. It is to be remembered that Jones reductors always give a greater blank in the first run after disuse for a short period, and that solutions which have been treated with hydrogen sulfide contain oxidizable polythionic acids which must be destroyed by permanganate before final reduction with zinc or stannous chloride.

DETERMINATION OF NICKEL—(1) For small amounts of nickel the glyoxime method is unquestionably the most desirable. The glyoxime should be added to the hot acid solution which is then made ammoniacal. This results in quicker precipitation with small amounts of nickel than is obtained by reversing the procedure and the precipitate is more easily filtered. Digestion of the warm solution for one to two hours before filtration is desirable and hot water is the most satisfactory wash.

(2) In case nickel dimethylglyoxime is ignited to the oxide, care must be taken to prevent sublimation of the undecomposed salt.

(3) The electrolytic method tends to give high values with small amounts of nickel, owing in part to solution of the anode and partial deposition of platinum on the cathode.

Method of Analysis

The most attractive method for the analysis of this type of material lies in a nitric acid attack followed by digestion and filtration to separate tin and antimony from the other elements. It is apparent, from what has been said, that the nitric acid filtrate must be examined for tin and antimony, while the nitric acid precipitate must be worked over for such contaminating elements as iron, copper, and zinc.

The following method calls for a nitric acid attack on two samples of bronze. In one sample, tin and antimony are filtered off, washed slightly, reserved, and then combined with any tin or antimony recovered from the filtrate. The tin and antimony are then put into sulfuric acid solution, the antimony is determined by titration with permanganate in the presence of hydrochloric acid, and the tin afterwards determined iodometrically in the same solution after reduction with test lead in an atmosphere of carbon dioxide. In the second sample, tin and antimony are filtered off, washed slightly, the filtrate is reserved, and then combined with a nitric acid solution of any contaminants recovered from the tin and antimony. Copper and lead are then determined electrolytically. Zinc is thrown out in the electrolyte as sulfide in 0.01 *N* sulfuric acid solution and ignited to oxide. Iron is then precipitated twice by ammonia and weighed as oxide. Finally nickel is thrown out and weighed as nickel dimethylglyoxime. It is thus apparent that the method calls for volumetric determinations of antimony and tin, the simultaneous electrodeposition of copper and lead, and gravimetric determinations of zinc, iron, and nickel. As is shown, the gravimetric determination of lead and volumetric determinations of zinc, iron, and nickel can be substituted without changing the main procedure.

Gravimetric methods for tin, antimony, and lead are not favored, in spite of the desirability of finally having in an analysis a compound which may be seen and tested. The gravimetric method for tin as SnO_2 is not specified on account of the impure character of the precipitate and the necessity of attempting corrections which, in the hands of novices, usually introduce greater errors than would the impurities. The volumetric method for antimony is preferred, in spite of the small amount present, on account of its rapidity and an accuracy equal to if not greater than that obtainable by ordinary care in a gravimetric determination as Sb_2O_4 or Sb_2S_3. The electrodeposition of lead is preferred in the absence of manganese and with the small amounts of lead involved, on account of the ease and rapidity of the method; there is no reason why lead cannot be separated and weighed as $PbSO_4$ prior to the electrodeposition of copper.

Determination of Antimony and Tin

Digest 3 g. of the sample with 50 cc. of nitric acid (sp. gr. 1.2) until decomposition is complete, boil to expel oxides of nitrogen, dilute with 150 cc. of hot water, and digest for 3 or 4 hrs. on the steam bath. Filter, keeping the solution hot, through a filter of close texture, and wash a few times with hot dilute nitric acid (1 per cent by volume). Reserve the precipitate. Nearly neutralize the filtrate with ammonia, pour the solution while stirring into an excess of ammonium sulfide, and digest at the side of the steam bath for an hour. Filter, wash slightly with water containing a little ammonium sulfide, and discard the precipitate. Acidify the filtrate with hydrochloric acid added in slight excess and digest at the side of the steam bath until the sulfur and sulfides settle. Filter, wash the residue with acidulated hydrogen sulfide water, and combine the paper and its contents with the reserved precipitate.[3]

ANTIMONY—Place the papers and precipitates in a 500-cc. Erlenmeyer flask and add 25 cc. of nitric acid (sp. gr. 1.42), 5 g. of ammonium persulfate, and 15 cc. of sulfuric acid (sp. gr. 1.84). Boil until strong fumes of sulfuric acid escape. If the solution is brown, cool, and add 5 cc. of nitric acid and 1 g. of persulfate, and boil again until strong fumes appear.[4] Cool, dilute to 40 cc., add 0.5 to 1.0 g. of sodium sulfite to reduce all of the antimony to the trivalent state, and boil until sulfur dioxide is expelled. Add 200 cc. of distilled water, 20 cc. of hydrochloric acid (sp. gr. 1.19), cool to about 10° C., and titrate with a standard solution of permanganate[5] to a pink tint which persists for 10 sec. The titration should be corrected by a blank determination (usually amounting to about 0.06 to 0.08 cc. of 0.1 *N* permanganate solution) carried out on a filter paper carried through all of the steps of the determination.[6]

TIN—Pour the titrated solution into a 500-cc. Erlenmeyer flask, add 80 cc. of hydrochloric acid (sp. gr. 1.19), and insert a 3-hole stopper carrying gas inlet and outlet tubes, and having the third hole closed by a small stopper. It is advisable to use an air condenser about 15 to 20 cm. in length in the gas outlet. Add 1 to 2 g. of test lead,[7] start a slow current of carbon dioxide from a Kipp generator or a cylinder, heat gradually to boiling, and boil gently for about 40 min. Finally cool in ice to about 10° C., after increasing the current of carbon dioxide in order to prevent back pressure. This may be detected by placing a bubbling tube in the gas outlet. When the solution is cold, take out the stopper in the third hole, add 5 cc. of clear starch solution from a pipet, and insert the tip of a buret containing standard iodine solution,[8] and titrate to a permanent blue tint. The titration should be corrected by a blank determination (usually amounting to 0.05 to 0.08 cc. of 0.1 N iodine solution) carried through the steps of the procedure.

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[3] In case the alloy does not contain much iron or antimony the above recovery may be safely omitted in routine analyses.

[4] This method of attack was used with success by the American Brass Company. At this Bureau the paper and precipitate are placed in a Kjeldahl flask, treated with 2 to 4 g. potassium sulfate and 20 cc. of sulfuric acid, and heated as in a nitrogen determination to complete solution of the sample and the destruction of organic matter.

[5] The permanganate solution should contain approximately 3.16 g. potassium permanganate per liter. The theoretical antimony titer (approximately 0.006) as calculated by standardization against oxalate may be used, although it is preferable when dealing with an alloy of high antimony content or in accurate work to standardize under like conditions against material of known antimony content.

[6] This determination is subject to interference by arsenic and vanadium. So far as is known to the authors, vanadium is not employed in this class of material. Its presence could be easily detected by a hydrogen peroxide test of the titrated solution and its interference avoided by precipitating tin and antimony by hydrogen sulfide in acid solution, filtering, and then putting the sulfides into sulfuric acid solution. As regards the interference of arsenic, its prior removal is attended by uncertainty and by danger of volatilizing tin and, particularly, antimony. Therefore with the small amounts ordinarily present (0.00 to 0.03 per cent), it is safer to titrate, calculate the apparent percentage of antimony, and then deduct 1.86 times the percentage of arsenic as separately determined. (The factor 1.86 takes into account the difference in the atomic weights of antimony and arsenic and also the excess of permanganate required to get an end-point with arsenic.) With larger amounts of arsenic a modification such as that of Stief, This Journal, 7 (1915), 211, is called for.

Determination of Copper, Lead, Zinc, Iron, and Nickel

Treat 5 g. of the sample as for the determination of antimony and tin, reserve the nitric acid solution, and treat the sulfuric acid solution of tin, antimony, and impurities with 10 g. of tartaric acid, and sufficient 10 per cent potassium hydroxide solution to neutralize the acid and redissolve the precipitate formed.[9] Pass in a stream of hydrogen sulfide for 10 to 15 min., dilute to 600 to 800 cc., and digest for 2 to 3 hrs. on the steam bath, or preferably let stand over night. Filter and wash slightly with warm 1 per cent sodium or potassium sulfide solution, being careful not to allow the precipitate to run dry lest iron sulfide be oxidized and lost. Rinse as much of the sulfides as possible from the paper into the original beaker, dissolve the sulfide adhering to the paper in a small amount of hot dilute nitric acid (1:1) and boil to complete solution of the sulfides. Combine the nitric acid recovery with the reserved nitric acid filtrate and proceed as below.

COPPER AND LEAD—Neutralize the nitric acid solution with ammonia, add 1 cc. of nitric acid (sp. gr. 1.42) for every 100 cc. of solution, and electrolyze, using a platinum gauze cathode and sand-blasted gauze anode in a beaker of tall form covered with split glasses. When deposition is complete as demonstrated by the ordinary tests, the cathode and anode should be thoroughly washed with water as the beaker is lowered. Reserve the electrolyte. Dry the cathode and anode in the usual manner, weigh, and calculate copper[10] and lead.[11]

ZINC—Evaporate the electrolyte and washings to small volume, add 10 cc. of dilute sulfuric acid (1 : 1) and heat to the appearance of fumes of sulfuric acid. Cool, dilute, treat with hydrogen sulfide, filter off any precipitate, and wash with dilute sulfuric acid (1 per cent by volume) saturated with hydrogen sulfide.[12] Boil off hydrogen sulfide, add 2 drops of methyl orange solution and neutralize with ammonium hydroxide. Finally, dilute to about 100 cc. for every 0.1 g. zinc and make 0.01 N with sulfuric acid (1 cc. N acid to every 100 cc. of solution). Precipitate zinc as sulfide in cold solution, using a rapid current of hydrogen sulfide. Filter, wash with cold water, reserve the filtrate, and ignite the wet filter and contents very slowly in an oxidizing atmosphere until all carbon is destroyed. Gradually increase the temperature to 850° for complete decomposition of the zinc sulfate formed. Do not heat above 900° C. Cool and weigh as ZnO.[13]

IRON—Boil the filtrate reserved from the zinc determination until hydrogen sulfide and sulfur are expelled, using a few crystals of ammonium persulfate toward the end. Add a few drops of methyl red and then dilute ammonium hydroxide (1 : 1) drop by drop until the color of the solution changes to a distinct yellow. Boil the solution for 1 to 2 min., filter at once without washing, and reserve the filtrate. Dissolve the precipitate in a small amount of hot dilute hydrochloric acid (1 : 1), reprecipitate with ammonia as before, filter, and wash slightly with hot ammonium chloride solution (2 per cent). Add this filtrate to the one already reserved. Ignite the wet paper and precipitate in a weighed platinum crucible in an oxidizing atmosphere, treat with a drop of dilute sulfuric acid (1 : 1), 1 to 5 cc. of hydrofluoric acid, evaporate to dryness, again ignite, and weigh as Fe_2O_3.[14]

NICKEL—Acidify the combined filtrates from the iron determination, evaporate to approximately 300 cc., and filter if not absolutely clear. Nearly neutralize with ammonia, warm, add an excess of a 1 per cent alcoholic solution of dimethylglyoxime, and make slightly ammoniacal. After warm digestion for about 1 hr., filter on a weighed Gooch crucible, wash with hot water, dry at 110° to 120° for about

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[7] Some analysts prefer reduction by metallic antimony, iron, nickel, etc. The authors have found test lead to be very satisfactory, as it does not reduce in cold solution and hence does not require removal.

[8] The iodine solution is prepared by dissolving about 12.7 g. of iodine in a solution of about 20 g. of potassium iodide in a little water, diluting to one liter, and standardizing against pure tin by the method described. The starch solution is prepared by allowing raw starch to stand for 24 hrs. in very dilute hydrochloric acid, filtering, washing, and drying at 100° C. for 3 hrs. One gram of the hydrolyzed starch is then made into a paste with cold water, poured into 100 cc. of boiling water, boiled for 3 min., cooled, and allowed to settle.

[9] In case antimony is absent, sodium hydroxide may be substituted for potassium hydroxide.

[10] If the material contains much iron or antimony, or the most accurate results are desired, the copper deposit must be examined and corrected for tin and antimony as follows: Dissolve the weighed deposit in nitric acid (1 : 1), add 0.01 g. of iron as ferric nitrate, boil, and precipitate with an excess of ammonia. Filter, wash the precipitate with hot water, and dissolve it in a small amount of hot dilute hydrochloric acid (1 : 1). Pour the solution, while stirring, into a moderate excess of potassium hydroxide solution (10 per cent), pass in a rapid stream of hydrogen sulfide, and digest for a few hours on the steam bath. Filter, wash the precipitate slightly with dilute potassium sulfide solution and render the clear filtrate faintly acid with dilute hydrochloric acid. Allow the solution to stand at the side of the steam bath until the precipitate settles, filter, wash the paper and precipitate thoroughly with acidulated hydrogen sulfide water, and dissolve as much of it as possible in a little hot dilute nitric acid (1 : 1), keeping the solution. Burn the paper at the lowest possible temperature in a tared crucible, add the reserved nitric acid solution, evaporate to dryness, and ignite at a red heat in an oxidizing atmosphere. Multiply by the factor 0.788 (which serves in these small amounts for both tin and antimony) and deduct from the weight of the copper deposit.

[11] The lead deposit may be contaminated by silica, tin, and manganese. The first two are not ordinarily serious; in the case of manganese or when much lead is present, it is safer to precipitate lead as the sulfate in the combined nitric acid solutions and then proceed with the electrolysis of copper.

[12] In accurate analyses the sulfides must be ignited, copper and lead determined, and proper corrections made. In routine analyses, they would be disregarded except when appreciable in amount.

[13] Instead of the prescribed gravimetric procedure, the washed zinc sulfide may, in routine analyses, be dissolved in hydrochloric acid and titrated under the necessary definite conditions with a ferrocyanide solution which has been standardized under the same conditions against material of known zinc content.

[14] The weighed precipitate will contain all of any aluminium that may have been in the bronze. The residue may therefore be examined for aluminium by fusing it with a little sodium carbonate, dissolving the cooled melt by digestion in dilute hydrochloric acid, reducing the almost neutral solution with a few drops of ammonium bisulfite and then testing with phenylhydrazine as in the method of Hess and Campbell, as modified by E. T. Allen [*J. Am. Chem. Soc.*, **25** (1903), 421].

Instead of the prescribed procedure, the final ammonia precipitate may be dissolved, reduced, and titrated. The advantage of the gravimetric procedure lies in the opportunity afforded for investigation of the character of the ammonia precipitate.

If iron alone is to be determined in the alloy, dissolve the weighed sample in aqua regia, boil, add ammonia in excess, and filter off the iron, lead, tin, and antimony. Dissolve the precipitate in a little hot dilute sulfuric acid, filter off any lead sulfate, and treat the acid solution with hydrogen sulfide. Filter, evaporate the filtrate to copious fumes of sulfuric acid, cool, and dilute. Finally add permanganate solution to a pink tint and proceed with the reduction and titration. The above method does not provide a satisfactory separation of aluminium on account of the large excess of ammonia which is necessary in the initial treatment.

2 hrs., and weigh, as the glyoxime salt, which contains 20.31 per cent nickel.[15]

ACKNOWLEDGMENT

The authors desire to express their indebtedness to Dr. W. F. Hillebrand for his interest and aid in the work.

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[15] In routine analyses the glyoxime precipitate may be filtered on paper, the wet paper wrapped in another moist "ashless" paper and then slowly and carefully ignited to NiO. It may also be dissolved in nitric acid and titrated with cyanide solution by the method of Frevert [A. A. Blair, "Chemical Analysis of Iron," 8th edition, J. B. Lippincott and Co., 182. See also G. L. Kelley and J. B. Conant, THIS JOURNAL, **8** (1916), 804].

The Analysis of Solutions of Ammonium Citrate[1,2]

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An investigation of methods of determining the ratio of ammonia to citric acid in ammonium citrate solutions points to two methods which can be relied upon to give accurate results. When properly carried out they give values which agree with each other and accurately represent the composition of the solutions analyzed.

In the formaldehyde titration method, the only precautions to be observed are that the formaldehyde shall be neutral and present in sufficient quantity to combine with all the ammonia.

In the other method the alkaline residue left after the distillation of the ammonia is made acid to methyl red with a measured amount of standard acid and titrated with standard alkali with phenolphthalein indicator.

IN the course of the study of the colorimetric method for the preparation of neutral solutions of ammonium citrate, undertaken while the senior author was associate referee on this subject for the Association of Official Agricultural Chemists, his attention was called to the diversity of procedures employed in the analysis of such solutions. As the determination of the ratio of ammonia to citric acid by analysis is one of the best ways of checking the reactions of ammonium citrate solutions the accuracy of the methods used is of considerable importance.

While referee on phosphoric acid in 1908, McCandless[4] used the determination of the ratio of ammonia to citric acid as the criterion of the reaction of solutions submitted to him. His procedure consisted of adding a measured amount of 0.25 N alkali to the citrate solution and distilling off the ammonia which was collected in a measured amount of standard acid and determined by titrating the excess acid. To the residue in the distillation flask he added "an excess" of 0.5 N acid and phenolphthalein and titrated back with 0.1 N alkali to the end-point. This procedure is apparently used in many laboratories either exactly as described by McCandless, modified as to the strength of solutions used, or by eliminating the last step and titrating the excess of the originally added standard alkali directly to a phenolphthalein end-point.

A second type of method is the so-called formaldehyde titration method suggested by Patten and Marti.[5] In this method the ammonia is removed from the sphere of action by causing it to combine with formaldehyde, as was done by Schiff.[6] The citric acid is then titrated directly to a phenolphthalein end-point.

Several collaborators claimed that they were unable to get these two types of methods to agree, and hence concluded that the second one was unreliable. Upon trying to check up the composition of some solutions by both types of methods the authors actually found that the results did not agree. However, as the formaldehyde method had been in use in this laboratory since it was first suggested and since it is in constant use in scores of other laboratories in biochemical work, the authors were skeptical as to its shortcomings. Hence the investigation of both methods was undertaken.

COMPARISON OF RESULTS

The first points studied were the agreement of these methods with each other and with themselves when used on the same solution. Needless to say, every possible precaution against error was taken. The reagents were all carefully standardized, using as a standard of reference 0.1 N HCl prepared by the method of Hulett and Bonner[7] and checked gravimetrically. The flasks and burets were all carefully calibrated. (This precaution should not be neglected. Burets have been purchased recently from reputable supply houses which upon calibration have been found to be as much as 0.4 cc. off, and variations of 0.1 cc. are common.)

The following procedures were studied:

1—The original technic of McCandless, with 0.25 N alkali for the initial stage, 0.5 N acid for the second, and 0.1 N alkali for the back titration.

2—The same technic as (1), but with 0.1 N reagents throughout.

3—The same procedure as (2), except that the addition of acid was continued until the solution was acid to methyl red.

4—Direct titration to a phenolphthalein end-point with 0.5 N HCl, after the addition of 35.00 cc. 0.5 N $NaOH$.

5—The formaldehyde method, with 0.1 N reagents.

The results are shown in Table I, page 430.

At the bottom of each set of determinations is shown the maximum variation among the individual estimations. It will appear at a glance that two of the methods, *viz.*, 2 and 4, give variations much larger than those in the other two methods. In calculating these variations all estimations have been considered. The proponents of these procedures will undoubtedly point out that this is unfair, since in some cases most of the figures agree fairly well, while only one or two differ materially from the rest. Thus, in the results by Method 2 on Solution II the second determination was a whole cubic centimeter lower than the next one to it. Were this result to be discarded, as, of course, it would be in practice, as being "off," the maximum variation would be reduced from 1.70 to 0.70. The same general statement applies to Determinations 4 and 5 by Method 4 on Solution II and 5 and 6 by the same method on Solution III. These results are,

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[1] Received January 12, 1922.

[2] Published as Journal Article No. 22 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

[3] Research Chemist, Michigan Agricultural College Experiment Station.

[4] *Bur. Chem., Bull.* **122**, 147; THIS JOURNAL, **6** (1914), 921.

[5] THIS JOURNAL, **5** (1913), 568.

[6] *Ann.*, **319** (1901), 76.

[7] *J. Am. Chem. Soc.*, **31** (1909), 390.

Table I—Comparative Results with Different Methods

Solution No.	Determination No.	Procedure No. 1	2	3	4	5
I	1	...	26.01	26.27	...	26.09
	2	...	26.19	26.17	...	26.18
	3	...	26.32	26.22	...	26.09
	4	...	26.46	...	...	26.19
Maximum variation		...	0.45	0.10	...	0.10
Average		...	26.25	26.19	...	26.14
II	1	27.38	30.23	27.27	30.70	27.20
	2	27.46	29.23	27.48	30.05	27.24
	3	27.38	30.93	27.48	30.05	27.30
	4	27.26	30.73	27.48	31.05	27.30
	5	27.38	30.53	...	29.55	27.24
	6	...	30.38	...	30.05	27.30
Maximum variation		0.20	1.70	0.21	1.50	0.10
Average		27.37	30.34	27.38	30.24	27.25
III	1	27.40	31.02	27.08	28.46	27.03
	2	27.30	31.85	27.58	28.26	27.08
	3	27.38	32.35	27.08	28.71	27.03
	4	27.53	31.72	26.93	28.67	27.03
	5	27.55	32.25	27.29	29.36	27.08
	6	27.51	29.64	27.18	27.07	27.03
Maximum variation		0.25	2.71	0.65	2.29	0.05
Average		27.44	31.47	27.19	28.42	27.05

however, given consideration because repeated tests have shown that such discordant results continually occur and are typical of the methods. In fact, the rather close agreement of the majority of the results is to be regarded as a very insidious danger in forming a correct opinion of their value. Thus the series given, which includes three perfect checks, would indicate that with perhaps a little care in manipulation good results might be had. Only a thorough investigation of the procedures themselves and the careful repetition of many determinations have shown conclusively that consistent results cannot be obtained.

Of the five methods given, 1, 3, and 5 evidently agree much better with each other than with the other two or than the other two do with each other. (The agreement of the results on Solution I by Methods 2 and 5 as well as those on Solution II by Methods 2 and 4 are fortuitous, as will be shown later.) This was rather unexpected, since Method 1 differs from Method 2 only in the strength of the solutions employed. The explanation, however, actually does lie in the fact that in the original technic of McCandless (Method 1) a strong solution of acid was used, *i. e.*, 0.5 *N*; hence the "excess" was so large that the reaction was carried far enough to reduce the discrepancies between this method and 3 to within the limits of experimental error. In Method 2, on the other hand, the use of 0.1 *N* acid causes a smaller excess to be added beyond the phenolphthalein end-point, with the result that the figures approximate those obtained by 4 rather than by the other procedures.

The uncertain point of the whole matter is the meaning of the term "excess of acid." McCandless, of course, meant an excess over the amount of alkali not neutralized by the citric acid. He apparently assumed, and very naturally since this was the end-point ultimately sought, that this point would be shown by phenolphthalein. Unfortunately this is not the case, for on approaching it from the alkaline side a pseudo-end-point is first encountered at which the color of the indicator is discharged although some of the alkali is still unneutralized. Only when the addition of acid is continued until the reaction of the solution is below a pH of about 5.5 is all of this excess alkali neutralized. The "excess acid" can then be titrated back with alkali and a true end-point with phenolphthalein reached. The proper reaction to be passed in the addition of acid can be determined by the use of methyl red instead of phenolphthalein as the indicator. Since methyl red is pink in acid solutions and straw-colored in alkaline ones it does not interfere with the use of phenolphthalein in the same solution.

Electrometric Titrations

In order to make the relationships more clear a citrate solution was prepared and analyzed by Methods 2, 3, and 5; the courses of the titrations were followed electrometrically with a hydrogen electrode. Method 2 was repeated several times, with the addition of varying quantities of acid intermediate between those required to give solutions acid to phenolphthalein and to methyl red. For instance, 8.50 cc. 0.1 *N* HCl discharged the phenolphthalein color and 20.00 cc. produced the pink of the methyl red. Four titrations were made, with the addition of 11.00, 12.00, 14.00, and 16.00 cc. of 0.1 *N* HCl, respectively, before titrating back to the final phenolphthalein end-point. The final figures for citric acid in terms of 0.1 *N* NaOH are given in Table II and the complete titration curves are shown graphically in Fig. 1.

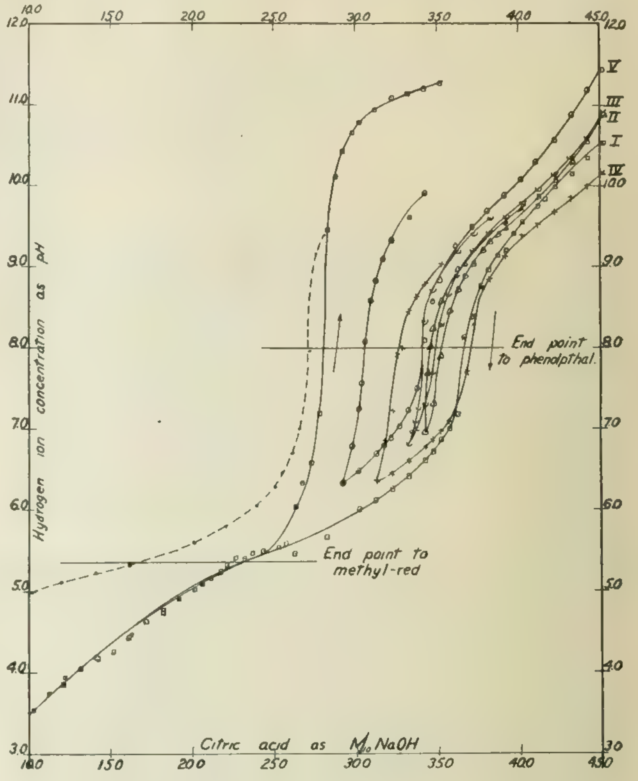

Fig. 1—Electrometric Titration of Citrate Solutions

Table II—Citric Acid in Ammonium Citrate Determined by Different Methods. Titrations with H Electrode

	Citric Acid
Method 2:	
11.00 cc. 0.1 *N* HCl	34.55
12.00 cc. 0.1 *N* HCl	34.23
14.00 cc. 0.1 *N* HCl	32.55
16.00 cc. 0.1 *N* HCl	30.64
Method 3	27.77[1]
Method 5	27.20[2]

[1] Not boiled after addition of acid.

[2] Several electrometric titrations were made by Methods 3 and 5 with results agreeing as well as by the titrations with indicator. The results are omitted because of the confusion caused by a multiplicity of closely agreeing curves.

In this figure the ordinates represent pH values. The abscissae represent the cc. 0.1 *N* NaOH added less the cc. 0.1 *N* HCl added. The addition of acid is therefore shown by a decrease in the total. Except in the solutions titrated by the formaldehyde method, a total of 45.25 cc. 0.1 *N* NaOH was added to the original solution and the ammonia boiled off. This gives the starting points for all the curves on the extreme right of the figure. The addition of 0.1 *N* HCl is shown by decreasing values for the total alkali present, carrying the curves to the left with decreasing pH values. The final back titration with alkali causes the reverse to take place, *i. e.*, the curves pass upwards and to the right. The titrations were carried out with the indicators present in the solutions and the points at which the colors changed were noted.

A study of the figure shows that with the addition of acid the reaction changes rather rapidly although the curves still show a distinct change in direction coinciding with the disappearance of the phenolphthalein color. This end-point is the one used in Method 4. The poor agreement of the several curves at this point is only an exaggeration of that obtained in practice, due perhaps to the longer time required to make the separate additions of acid in the electrometric titration. Occasionally, as in the cases of Curves I and IV, perfect agreement is obtained and generally, as in the cases of Curves II, III, and V, the differences are within a range of 1 cc., but these differences are not accidental.

The situation as regards Method 2 is illustrated by the upward branches of Curves II, III, IV, and V. The end-points here follow strictly the order of the amounts of acid added, 11.00, 12.00, 14.00, and 16.00 cc. of acid used giving values for citric acid corresponding, respectively, to 34.55, 34.04, 32.55, and 30.64 cc. 0.1 *N* NaOH. Evidently the closer the amount of acid added approaches that required to give a pH of 5.5 the more closely will the results agree with those of Method 3 and the formaldehyde method. So in the case of McCandless' original technic the use of a concentrated acid caused the reaction to be carried so far that in its backward course it came very close to the true end-point.

It is to be observed that these curves differ from Curve I, in which a true excess of acid is added, in that the addition of alkali causes a sharp rise in the pH to the end-point. There is no "tail" as there is in Curve I along which the curves for the addition of acid and alkali coincide. This is but one sign of the general instability of the solutions in the range between the end-points with the two indicators. In this range there is always, on allowing the solution to stand, a "drift" in the potentiometer readings towards the alkaline side, an apparent tendency for the reaction spontaneously to get up to the reflex part of Curve I. It is this condition of unstable equilibrium which is responsible for the discordant results afforded by Methods 2 and 4 and to a lesser extent by Method 1. Even the quantity of alkali initially added has its effect, as is shown by Table III, which gives the results of analyses by Method 2, using different amounts of alkali to drive off the ammonia.

TABLE III—EFFECT OF ADDITION OF DIFFERENT AMOUNTS OF ALKALI ON CITRIC ACID VALUES BY METHOD 2

Solution	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Citric Acid by Formaldehyde Method
I	28.00	27.50	34.98	29.47	44.92	31.39	27.30
	28.00	27.50	34.98	29.77	44.92	33.49	
	28.00	27.50	34.98	29.97	44.92	32.99	
II	28.00	24.99	34.98	26.66	44.92	25.70	24.31
	28.00	24.99	34.98	27.36	44.92	25.50	
	28.00	25.10	34.98	27.76	44 92	25.80	

Other factors may, however, predominate, as in the last set of values for Solution II, which were made the day following the carrying out of the other analyses and presumably with some difference in manipulation. Only with Method 3 of this type of procedure can consistent results be had, irrespective of the above-discussed conditions. Table IV illustrates the independence of Method 3 of the amount of alkali originally added.

TABLE IV—EFFECT OF ADDITION OF DIFFERENT AMOUNTS OF ALKALI ON CITRIC ACID VALUES BY METHOD 3

Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Citric Acid by Formaldehyde Method
28.00	24.45	34.98	24.44	44.92	24.47	24.31
28.00	24.55	34.98	24.33	44.92	24.48	
28.00	24.54	34.98	24.33	44.92	24.28	
Av.	24.51		24.37		24.41	

The question may still be raised: Do the figures obtained by these two methods actually show the composition of citrate solutions or do the true values lie in a region near the grouping of curves of Method 2 in Fig. 1? One collaborator stated that his reason for preferring Method 2 to 5 was that the former method, when used on a solution made to contain certain quantities of ammonia and citric acid, gave results agreeing more closely with the calculated values than did Method 5. This is entirely contrary to our experience. The question involved can be answered in the following manner:

The one solution of ammonium citrate having a known and definite ratio of citric acid to ammonia, which can be prepared without the help of any method of analysis, is a solution of the normal triammonium citrate. Such a solution can be prepared by neutralizing citric acid with ammonia by (1) the electrical conductivity method,[8] (2) the temperature method of Bell and Cowell,[9] and (3) by the electrometric titration method with a hydrogen electrode.[10]

In such a solution the ratio of ammonia to citric acid will be 1:3.759. Two such solutions were prepared using the first and third methods on each. They were analyzed by Methods 4 and 5. The results are given in Table V.

TABLE V—RESULTS OF ANALYSIS OF SOLUTIONS OF TRIAMMONIUM CITRATE BY METHODS 4 AND 5

Solution	Ratio NH_3: $C_6H_8O_7$ Method 4	Method 5
A	1 : 3.966	1 : 3.750
B	1 : 3.950	1 : 3.763

These figures are averages of six separate determinations of citric acid and ammonia by each method. Patten and Marti in their original article on the formaldehyde method likewise report the analysis of such a solution giving a ratio of 1:3.765. When it is recalled that a variation of 0.1 cc. 0.1 *N* reagent in the determination of either ammonia or citric acid makes a difference of approximately 0.015 in the ratio, the deviations of the results by Method 5 from the theoretical value are seen to be well within the limits of experimental error, and they leave no question as to which method gives the true composition of citrate solutions.

SUMMARY

Of the methods for the analysis of solutions of ammonium citrate discussed in this paper only two can be relied upon to give accurate results. When properly carried out they give values which agree with each other and which accurately represent the composition of the solutions upon which they are used.

One of these is the formaldehyde titration method. The only precautions to be observed in this method are that the formaldehyde shall be neutral and present in sufficient quantity to combine with all of the ammonia. The addition of alkali is carried to the first permanent pink of the indicator which should be present in sufficient quantity to give a distinct color.

The other procedure is carried out as follows, with solutions of the concentration ordinarily used in fertilizer analyses:

Fifty cc. of the original citrate solution are diluted to 500 cc. in a volumetric flask. Ten-cc. samples of this solution are measured in Kjeldahl flasks, an excess of standard alkali added, and the ammonia distilled off and titrated in the usual manner. The residue in the distillation flask is transferred to a suitable flask or beaker, some methyl red added and then standard acid until the solution is acid as shown by the appearance of the red color of the indicator. No precautions need be taken against over-running this end-point as an excess of acid is desired. The solution is then boiled to expel carbon dioxide and the excess acid titrated with standard alkali after the addition of phenolphthalein. The difference between the total alkali and acid used gives the amount of alkali neutralized by the citric acid in the sample.

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[8] *J. Am. Chem. Soc.*, **33** (1911), 711. THIS JOURNAL, **4** (1912) 443; Mich. Agr. Expt Sta., *Tech. Bull.* **12.**

[9] *J. Am. Chem. Soc.*, **35** (1913), 49

[10] *Ibid.*, **36** (1913), 857.

Determination of Suspended Impurities in Gases[1]

By Wilfred W. Scott[2]

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Beam Test

Tyndall demonstrated that dust particles are responsible for the visibility of rays of light, such as the sunbeam or the beam of the searchlight. He did not make clear the best conditions enabling one to see the beam produced by minute amounts of suspended matter in purified gases, nor did he show that a gas free of dust may still produce a beam in presence of liquid mist. The opinion commonly current regarding the conditions necessary to see the beam produced by light rays in purified gas, is that the rays should be parallel and should be viewed with the visual axis at right angles to this beam. Observing these conditions the author failed to see the beam when using direct sunlight, but discovered that a cone of light from an arc light gave a distinct beam. This led to the discovery that the beam is best viewed by glancing towards the source of light. Accordingly the apparatus shown in Figs. 1 and 1*a* was designed.

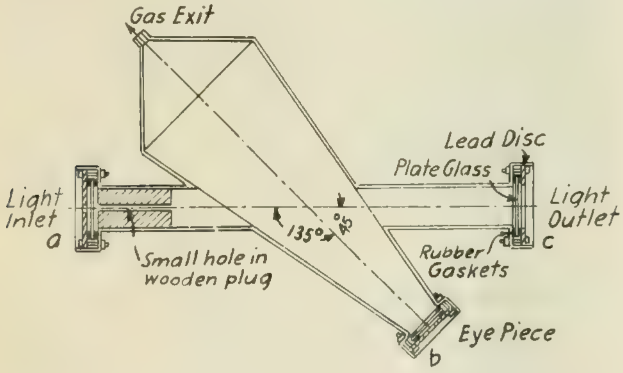

Fig. 1

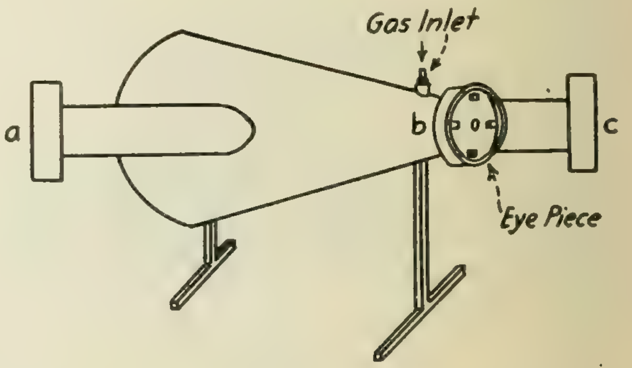

Fig. 1*a*

For the examination of a corrosive gas, it is advisable to have the chamber of the camera made of a material not affected by that gas. For example, in examining purified contact gas a lead chamber is recommended. The interior of the chamber is blackened with dull paint that is a poor light reflector. In the apparatus shown, circular glass disks close the ends of the tubes *a*, *b*, and *c*. The gas examined enters near the eyepiece *b* and passes out at the opposite large end. The ray of light is directed through a small opening, either circular (diam. 1 cm.) or a narrow slit, located at *a*, and passes through the arm of the tube and out through a glass window at *c*. The idea is to avoid light reflection in the chamber, as this would cause a glow in the tube and greatly reduce the sensibility of the test.

The beam caused by liquid mist alone appears as a uniform pencil or band of light, whereas dust particles produce a sparkling effect or irregular flashes of light. The beam is more intense with the gas in motion. Within certain limits the intensity of the beam is directly proportional to amount of suspended matter in the gas.

If the gas is dry the beam is completely removed by passing the gas through a 3-in. mat of loosely carded purified asbestos. If the gas, thus purified of solid matter, is passed through a liquid the beam again becomes apparent. From this it is evident that the test must be applied to dry gas if it is desired to ascertain the presence of solid matter in suspension.

Fig. 2 shows the apparatus set up for ascertaining the effectiveness of a scrubber in a quantitative determination of the solid and liquid suspended matter in a gas. The apparatus is so arranged that comparisons may be made of the unfiltered gas, by means of a bypass with that of the filtered or purified gas. Advantage is taken of the difference in pressures at A and B, so that a continuous sample may be taken of the gas without the necessity of an aspirator. A hand arc light shown on the left furnishes the rays of light which enter at *a* and pass out into the air at *c*. The beam is viewed through the eyepiece *b*. The meter measures the volume of gas aspirated.

Determination of Solid and Liquid Impurities

Solid or liquid impurities suspended in a gas may be removed quantitatively by passing the gas through a filter of loosely carded dry asbestos. A filter 2 in. thick and 1.25 in. in diameter is effective in removing suspended matter completely with gas passing through it at the rate of 2 to 3 l. per sec. (5 to 7 cu. ft. per min.). It is essential that the asbestos be free from condensed moisture as a soggy filter is not effective for gas filtration.

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[1] Received March 3, 1922. Published by courtesy of D. Van Nostrand Co., New York, N. Y.

[2] Associate Professor of Chemistry, Colorado School of Mines; Editor of "Standard Methods of Chemical Analysis."

DETERMINATION OF SULFURIC ACID MIST IN GAS—The gas is aspirated through a filter of well-carded, blue fiber, purified asbestos, the asbestos extracted with water and the extract titrated with standard alkali.

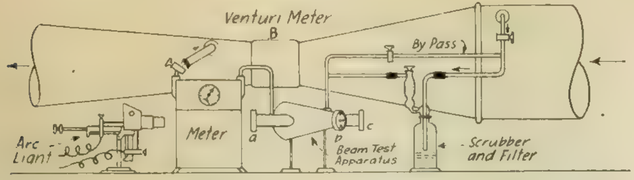

FIG. 2

APPARATUS—An ordinary 1.25-in. filter tube funnel (see Fig. 3) with long stem, to permit a sample being drawn directly from the flue, may be used. If the gas is supersaturated with moisture it is advisable to use the form of apparatus shown in Fig. 4, the bottle serving as a condensing chamber to avoid water condensation on the asbestos. Occasionally it is necessary to pass the gas through two such chambers to remove the condensed moisture from warm moist gases.

The funnel is packed first with a layer of glass wool, followed by a two-inch layer of well-carded, purified, blue asbestos, and finally a second layer of glass wool. The glass wool prevents the asbestos plugging the inlet and exit openings. Perforated disks may be used in place of the glass wool.

The asbestos is the blue African form. White asbestos will not give accurate results, as this is attacked slightly by dilute sulfuric acid and decidedly so by strong sulfuric. The blue form is not appreciably attacked, so that the acid may be extracted as free acid by water. The asbestos is purified by digesting with nitric acid, followed by a second digestion with hydrochloric acid. The material is now thoroughly washed to remove the acids and is dried. The dry asbestos is placed in wide-mouthed bottles until required. Before using it is carded or fluffed out by means of a pick and then placed loosely in the funnel to be used in the test.

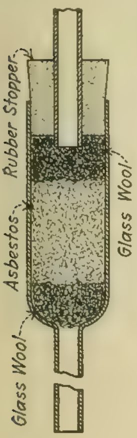

FIG. 3

Asbestos	SiO_2	CaO	MgO	FeO	Al_2O_3	MnO	H_2O
Blue African	49.0	1.2	2.7	24.4	11.9	..	..
White Canadian	40.3	..	43.4	0.9	2.3	..	13.7
White Italian	55.9	17.8	20.3	..	4.3	1.1	..

THE TEST—The gas is aspirated through the filter at the rate of about 5 cu. ft. per min., the gas being measured by a dry gas meter following the apparatus. When a volume of 10 to 100 cu. ft. of gas has been aspirated, the amount depending upon the amount of acid mist present in the gas, the asbestos filter is placed in a beaker. (If SO_2 is present in the gas, as is the case in contact sulfur gases, air is first passed through the asbestos to remove the SO_2.) The tube is rinsed out, and the rinsings poured on the asbestos. The contents of the the beaker are now transferred to a 2-in. Büchner funnel in position on a half-liter capacity suction bottle. The water is drawn out of the asbestos and the filtrate passed through the mat, thus formed, to remove the asbestos fibers. The mat is washed with small portions of pure water until free of acid, and the extract, transferred to a beaker, is titrated with standard alkali (0.05 *N* has been found to be satisfactory). Methyl orange is used as an indicator.

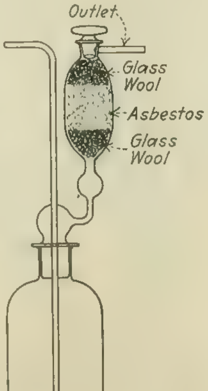

FIG. 4

DETERMINATION OF ARSENIC IN GAS—The test is the same as the one described for determining sulfuric acid. An aliquot portion of the water extract is taken for a Gutzeit determination of arsenic. Arsenic in purified contact gas is carried in the acid mist.

DETERMINATION OF CHLORIDES—A portion of the water extract, obtained by the procedure described under the test for acid in gas and filtered through paper if necessary, is examined for chloride by the turbidity test by addition of nitric acid followed by silver nitrate reagent. Comparison is made with a standard using either Nessler tubes or a colorimeter. If the amount of chloride is too great for a turbidity test a gravimetric determination should be made, or the aliquot portion taken should be sufficiently diluted with water to enable the turbidity test to be made. The standard should contain the same amount of sulfuric acid as the sample. The extract should be free of asbestos fiber.

Liquid Oxygen Explosives

Although the use of liquid oxygen explosives has not yet made much headway in the United States, experiments made with such explosives by a metal-mining company at Pachuca, Mexico, operated by American capital promise quite satisfactory results, according to observations made by a representative of the United States Bureau of Mines. From the beginning of the entrance of the United States into the World War, efforts have been made by George S. Rice, Chief Mining Engineer of the Bureau of Mines, to have liquid oxygen explosives tried out practically in this country. Owing to the fact, however, that no manufacturer in the United States makes oxygen liquefying plants, the use of these explosives in America has been quite limited. The development of this innovation so far has been largely German, and in Germany oxygen liquefying plants are manufactured in various sizes in complete units of apparatus and containers.

Since the war the only extensive development outside of Germany has been in the Lorraine iron mines where the Germans installed apparatus, and additional apparatus has been put in by the French. One company in Lorraine is mining its entire annual output of 1,500,000 tons of iron ore by the use of these explosives. This company has developed a cartridge of its own on which it has received patents, and has applied for others. It is claimed that the cartridge is an improvement on the German cartridge. The Germans use for brisant effects, soot; and for slow heaving effects, wood pulp. Either fuse or electric detonators can be used for igniting the charge. The Germans have now developed a method of placing the electric detonator in the bottom of the hole in a special container and have been able to fire large rounds, it is claimed as high as twenty-eight shots at a time.

Fastness of Dyes

The National Council of Dyes and Colors held a meeting in New York City on March 20 and elected Mr. David N. Mosessohn of the Associated Dress Industries of America, permanent chairman. The secretary, Dr. J. Merritt Matthews, proposed that something of a definite and concrete nature should be undertaken by the Council and proposed that each of the industries interested and associated with the Council should definitely formulate the various staple fabrics in which they are particularly interested and state what qualities of colors with respect to fastness or other properties should normally be expected on these fabrics, so that data would be available regarding the commercial requirements for colors on fabrics. As a result, a motion was passed instructing the secretary to write to the representatives of the various industries to secure definite data as to the qualities of fastness required on the different staple fabrics and to present a report at the next meeting of the Council if possible. It was also voted to distribute 4000 reprints of Mr. Haynes' report on certain tests made on colored fabrics.

Wool Scouring Wastes for Fertilizer Purposes[1]

By F. P. Veitch[2]

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THIS country uses more than 600,000,000 lbs. of unscoured wool annually. Approximately half this weight consists of dirt, salts, grease, and albuminous and other organic matter which must be removed by careful washing. With the exception of the grease recovered at a few of the scouring plants, all of this material is wasted, being run into the streams of the country, seriously polluting the waters and rendering them unfit for domestic and many industrial purposes without purification at great expense.

Analyses of a large number of samples of all grades of unscoured wool, both domestic and foreign, show that the grease content varies from 6 to 42 per cent, averaging 14 per cent; that the water-soluble matter varies from 6 to 33 per cent, averaging 14 per cent; that the nitrogen (other than that of the wool) varies from 0.3 to 1.1 per cent, averaging 0.6 per cent; and that the potash varies from 1 to 7 per cent, averaging 4 per cent.

Both the potash and the nitrogen compounds are water-soluble, and it is these and the other water-soluble constituents of wool that are of interest as fertilizer materials.

Under present conditions, the wool scouring plants of this country are wasting annually potash equivalent to approximately 100,000 tons of Kainit, worth at present quotations $840,000, and 42,000 tons of 4.5 per cent tankage, worth $280,000 to the fertilizer manufacturer.

A number of attempts have been made both in this country and abroad to recover potash salts and other valuable constituents from wool scouring waste, but apparently without success, except for the relatively small proportion of grease that is being recovered by the centrifugal, cracking, and extraction processes. The problem should not be regarded as hopeless, however. It is believed that wool scouring wastes can be utilized at a profit, and that before long some procedure other than running them into the water courses of the country must be developed. In fact, some of the states are now very active in protecting water courses against pollution by trade wastes, especially against wool scouring wastes, which are among the most offensive and injurious. Wool scouring plants must purify their waste wash water at great expense and with little, if any, compensation from the sale of recovered products.

It is with the hope of working out economical processes for the recovery and utilization of all the useful constituents of wool scouring wastes that these investigations were begun by the Bureau of Chemistry. The cordial coöperation of the wool scouring industry on the one hand and of the fertilizer manufacturer on the other, without which the work cannot be carried to a successful conclusion, is sought.

Experiments have been conducted on a manufacturing scale in mixing concentrated wool scouring wastes with other waste materials for the purpose of determining the practicability of economically handling the material in the fertilizer factory. The material gave no trouble and the fertilizer manufacturer is ready to use the material as soon as it can be obtained in quantity, and, of course, at a price that will yield him a profit. "Base goods" have also been prepared on a factory scale, using the concentrated wool scouring liquors as the source of part of the potash and nitrogen. These experiments have also shown clearly that there is no difficulty in working the liquors in making base goods. Experiments to emphasize the agricultural value of the waste for fertilizer purposes are also in progress.

The concentrated liquid wool scouring waste liquor so far made contains 42 per cent of moisture, 14 per cent of K_2O, 1.25 per cent of nitrogen, and 14 per cent of grease, while the dried and degreased waste contains 24.5 per cent K_2O, 25.5 per cent nitrogen, and 0.6 per cent of grease. Fertilizer material made from the concentrated waste and another waste material on a factory scale contains 6.5 per cent water-soluble K_2O, 6.1 per cent total nitrogen, 3.4 per cent water-soluble nitrogen, 1.9 per cent alkaline permanganate-, and 1 per cent neutral permanganate-insoluble nitrogen, and 6.8 per cent of grease. This material is in excellent mechanical condition, may be handled easily in fertilizer mixing and grinding machinery, and in addition is a good dryer, with a dark color and a fine strong odor.

The work that has so far been done strongly indicates that wool scouring waste can be readily handled by the fertilizer manufacturer, giving him another source of potash, nitrogen, and filler of excellent quality, in an advantageous form. The farmer, the fertilizer manufacturer, the wool scourer, and the people and industries in the vicinity of wool scouring plants will benefit directly or indirectly from the recovery and utilization of the valuable but offensive and dangerous waste if it can be recovered economically. This, one of the most important points, is now being investigated with every hope of success, provided the cordial coöperation of the wool scourers and the fertilizer manufacturers can be had. So far the response of these industries has been most gratifying.

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[1] Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Chemist in Charge, Leather and Paper Laboratory.

Reversion to Generalized Types

By H. W. Jordan

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Throughout industrial America hundreds of graduate chemists and engineers, ousted from their modern, specialized industries by economic readjustment, following victory in the chemists' world war, have reverted to ancient, generalized commerce.

Some who were fortunate enough to own their homes are piecing out meager commercial incomes by discharging the servant and renting spare rooms. Others have sold their homes and have condensed their families within two boarding-house rooms. To make a living they are selling life insurance and unlisted bonds; dish drainers and sewing machines; ice cream pies and near-silk underwear. In plodding from house to house, these industrially insoluble scientists are making a lot of social analyses upon which they will report in due season.

"Specialization is always preparation for destruction. Although representing adaptation to existing conditions, it becomes inadaptation so soon as those conditions change," said Lester F. Ward, pioneer of American sociology in his classic work, "Pure Sociology," written twenty years ago. "The law of the persistence of the unspecialized is only the counterpart of the law of extinction of the specialized. What we have in the living flora of the globe to compare with those great fallen races of the past is merely the persisting, unspecialized types which escaped destruction simply because unspecialized," he adds.

Unless we chemists and engineers broaden our field of remunerative work by research and practical scientific activity in cultivation of social, economic fields, it is back to the dish drainers and sewing machines for us.

The Evaluation of Gelatin and Glue[1]

By Robert Herman Bogue[2]

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A need exists for standardization in gelatin and glue testing. The discussion of methods in the following paper indicates that this need arises from the failure of present methods to evaluate the material correctly, from lack of standard procedures for measuring properties, and from the absence of a scientific method of expressing the data which are obtained.

The gelatin content of glue or gelatin, and also the joint strength of a glue, may be correctly indicated by a melting point determination; neither may be assumed to be, in all cases, proportional to jelly consistency or to viscosity at 60° C. The measurement of the viscosity of an 18 per cent solution (dry basis) at 35° C. by means of the MacMichael viscosimeter has been shown to be especially well adapted as an indirect estimation of the differentiation of glues and gelatins in the order of their melting points, and is recommended as the basis for the primary evaluation of these products. Tests of jelly consistency and viscosity at 60° C. are of value in secondary evaluation, in determining the adaptability of a given glue to a given service. Other special tests are of course of value, but methods should be stated and a uniform method of expressing results should be adopted.

A system of designating the grade of a product, based on the results of this viscosity, is outlined in the paper.

VERY few substances which are extensively employed in the trades and the arts offer so much embarrassment to either the layman or the chemist in defining, or specifying, or testing their quality or purity as do gelatin and glue. Many factors contribute to this situation. Commercial gelatin and glue are by no means definite substances, and simple tests for purity are not available. Tests which are believed by one set of individuals or manufacturers to be comprehensive and indicative of certain fundamental properties are regarded as inadequate or untrustworthy by another set. Moreover the uses for which the various gelatins and glues are employed are so divergent that tests or analyses which may be entirely adequate for some given service would be quite useless as an indication of the value of the material for some other service.

The United States Bureau of Chemistry[1]* in 1910 accepted Fernbach's[2] statement that chemical analysis gives little information in regard to the value of a glue except in a few isolated and unimportant instances. The tests described by the Bureau of Chemistry *Bulletin* are moisture, ash, reaction, gelatin (nitrogen × 5.56), water absorption, viscosity (Engler), jelly strength (Lipowitz method), and melting point (by Cambon's fusiometer). Several of these tests are certainly obsolete. Nitrogen times a factor means nothing and is misleading, unless the sample be pure unhydrolyzed gelatin, which is almost never the case. Water absorption varies with too many incidental factors, and has little significance. The Engler viscosity test, the Lipowitz jelly strength test, and the Cambon melting point test have largely been replaced in most laboratories by more recent methods or apparatus.

PRESENT METHODS

The procedures in current use for the evaluation of gelatin and glue are based *primarily* upon the jelly consistency at low temperatures or the viscosity at high temperatures, and *secondarily* upon other incidental characteristics which depend upon the service for which they are designed. The Peter Cooper system of grading may be taken as typical of American practice. Because this system was the earliest recognized attempt at glue grading in this country, and has been in continuous service since its inception in 1844, it is recognized as a kind of American standard to which other glues produced by other houses may be referred in terms that will be at least partly intelligible to the professional glue buyer. The various manufacturing houses use symbols, however, expressive of their several grades, which are more or less zealously guarded as a kind of relic of alchemic mystery, but the consumer is enlightened upon their meaning only to the extent of learning that the glue in question is equivalent in jelly strength, for example, to the Peter Cooper grade $1^3/_8$, or equivalent in viscosity to the Peter Cooper grade $1^1/_4$. Thus the Peter Cooper system may be looked upon as a standard for reference.

Alexander[3] has proposed the substitution of figures varying by ten points each for the symbols of Peter Cooper, and has defined the jelly strength in ounces and in grams at 10° C. (measured by his jelly strength tester) to which the numbers correspond. The viscosity test (as measured by his instrument) is also used by him.

Table I expresses this system of grading:

TABLE I—ALEXANDER'S GLUE STANDARDS

STANDARD	Peter Cooper Grade	Viscosity 80° C.	Allowable Variation in Viscosity	JELLY STRENGTH In Oz. 10° C.	In G. 10° C.
10	...	15.5	± 0.25	...	....
20	...	16	± 0.25	...	....
30	2	16.5	± 0.25	...	....
40	$1^7/_8$	17	± 0.25	60	1701
50	$1^3/_4$	18	± 0.5	82	2324
60	$1^5/_8$	19	± 0.5	104	2948
70	$1^1/_2$	20	± 0.5	126	3572
80	$1^3/_8$	21	± 0.5	148	4196
90	$1^1/_4$	22	± 0.75	170	4820
100	1 X	23	± 0.75	192	5443
110	1	24	± 0.75	214	6067
120	1 extra	25	± 1	236	6691
130	A extra	26	± 3	258	7314
140	...	28	± 5	...	....
150	...	34	± 8	...	....
160	...	40	±12	..	....

Kahrs[4] in 1898 proposed a rather radical departure from the then existing (and still existing) disposition on the part of glue manufacturers to grade their product by tests which were intelligible and valuable to the buyer. He urged the adoption of four tests, *i. e.*, adhesion, economic value, cohesion, and congealing point. By *adhesion* he meant the viscosity, which was expressed in terms of the weight of dry glue necessary to make up 100 unit weights of the liquid material of the proper viscosity for application in joint work. This figure Kahrs found to vary from 29 to 60. That is, in the highest grade of glue a 29 per cent solution, and in the lowest grade a 60 per cent solution, was required to give a liquid of the correct consistency at about 60° C. for service in joining work.

The *economic value* was obtained by multiplying the adhesion value by the price per pound of the glue in question, and represented therefore the price of 100 lbs. of the liquid glue ready for application. Thus at 18 cents for the highest and 5.5 cents for the lowest grades (Kahrs' figures) the cost per 100 pounds of the liquid glue would be 18 × 29 = \$5.22 for the highest grade and 5.5 × 60 = \$3.30 for the lowest grade.

The *cohesion or strength* was measured by the crushing strength of the glue jelly made up at the concentration found under adhesion, and at a temperature of 65° F. (about 18° C.). The high temperature was used as it more nearly approached the temperature at which the glued joints would be used. This test was later substituted in part by an actual joint strength test.

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[1] Read at the Symposium on Gelatin and Glue before the New York Section of the American Chemical Society, New York, N. Y., January 6, 1922.

[2] Industrial Fellow of the Mellon Institute of Industrial Research of Pittsburgh, and Research Chemist for Armour and Co., of Chicago.

* Numbers in the text refer to Bibliography at end of paper.

The *congealing point* was measured as the temperature at which the glue, made up in the concentration indicated by the adhesion test, congealed to a jelly. This was found to vary from 91° to 75° F. and the interval of 16° was divided into ten "setting grades."

The test of the glue was then expressed somewhat as shown in Table II.

Table II—Kahrs' Glue Tests

Number	Price per Lb., Cents	Adhesion (Wt. per 100 Lbs. Standard Liquid)	Economic Value (Price per 100 Lbs. Liquid)	Cohesion (Strength)	Congealing Point
2942	18	29.3	$5.27	25	91.7
2924	5.5	57.8	$3.18	15	77.5

There are many interesting points in such a system. The table will show that although the first glue costs more than three times as much as the second, per pound, yet per unit volume of liquid ready to use it costs only six-tenths more. But it is shown to be worth more in producing, at that dilution, a greater strength, and in setting at a higher temperature, *i. e.*, more rapidly at any given temperature. Such a system enables one to see at a glance exactly wherein the differences in the glues lie, and to form an intelligent basis for judging between them. It at least gets down to salient and understandable data, which is much more than can be said for some systems now in use.

Thiele[5] bases the commercial value of edible gelatin on its viscosity (Engler), melting point, and color value.

PRIMARY AND SECONDARY TESTS—There is a difference of opinion as to what test should be regarded as the most *fundamental.* In Germany the viscosity test proposed by Fels,[6] made by the use of the Engler viscosimeter at 35° C., seems to be in greatest favor. In Italy a combination of viscosity and melting point is used.[7] In France and England the viscosity test and the melting point test by Cambon's fusiometer are employed. In this country the jelly consistency or strength is probably more used than any other test, although the viscosity test is in favor in many houses, and the melting point test by various methods is used. The quality of the material and the price are primarily rated upon these tests—sometimes a single one, and sometimes a combination of two or more. Clayton[8] concludes that the "observations seem to show that while it would be rash to form a judgment on glue from a single test, the evidences afforded by a number may be irresistible. The expert's surest system appears to be, not to rely on single short-cut tests of general quality, but to employ a number of methods including any having special bearing on the prospective or present uses of the glue, and then to base his conclusions on a consideration of all the results together." And Alexander[3] who cites the above, adds, "The truth of the matter is that the figures have a partial value, and then only to a glue expert." That is precisely the situation that the chemist should set himself to eradicate. Figures which mean little or nothing should be substituted if possible by data which do mean something, and which persons other than glue experts may comprehend.

The *secondary* basis for glue or gelatin evaluation lies in many or few other tests which are employed to determine the *applicability* of the material for any special service. For example, where the glue is to be used in mechanical spreaders, the tendency to foam is undesirable, and the foam test is of value. If the glue is to be applied by hand, the foam test is of little or no significance. If the glue is for use on paper as a size or on wall paper as a binder for the clay filler, grease should not be present in large amount, because it would form little droplets, making elliptical "eyes" or spots on the paper. In admixture with certain dyes the presence of acid or alkali is not permissible as the dye would be affected in one way or another. Suitable tests must accordingly be made upon glues designed for such purposes. Gelatin for use in photographic films or in printing rollers must have high jelly strength; if used for food or medicinal purposes it must be free from harmful impurities; if used in making marshmallows or other emulsions, a high viscosity and foam are desirable. Such a list could be greatly extended, and the *adaptability* of any glue or gelatin for its several uses is largely determined by such *secondary* tests.

The influence which such properties should exert upon the selling price of the product should be proportional, however, only to the extra cost involved in manufacturing any specialized type of material, and on the laws of supply and demand. If an extra clear glue is required the consumer should be properly expected to pay for the extra cost of clarification and filtration, and such extra cost should properly be figured on a sliding scale, dependent upon the final color and clarity, to be added to the cost of the untreated glue of the corresponding grade. For the textile trades where precipitation with alum must not occur; for veneer glues where foam is very objectionable; and for all other trades requiring glues of specific properties, the price should similarly be based upon a sliding scale to be applied to the market price of the regular corresponding grade. Where no extra cost is involved in the production of a specified glue, the sliding scale may apply according to the usual dictum supply and demand, but *it would seem most expeditious to base all such variations upon a standard primary evaluation.*

Diversity of Current Tests

The very large number of tests that have been used or proposed for carrying out the desired or required measurements makes it impossible at this time properly to discuss each and bring out the several merits and disadvantages attendant upon their use. In order, however, that some conception may be had of the extent and diversity of the proposed methods, a brief compendium may not be out of place.

For the measurement of jelly consistency, the finger test,[9] made by pressing the fingers on the jelly and comparing the firmness with that of a standard jelly under identical conditions, is still highly regarded by some testers. Of the early instruments proposed, the one designed by Lipowitz[10] in 1861 is still much used. The test consists in adding shot to a funnel, placed over a piston resting on a jelly, until the piston is forced nearly to the bottom of the glass, and the result expressed in terms of the weight of shot plus the weight of the apparatus. Kissling[11] noted the time taken by rods of different metals to sink through the jelly. Valenta[12] used a modified form of the Lipowitz instrument. Scott[13] forced a rod, terminating in a conical metallic head, into a jelly placed on a spring balance, and measured the deflection of the pointer at the moment the surface of the jelly was broken. Alexander[3] forced a cylindrical brass cup down upon a block of jelly, in the form of a truncated cone which had been removed from its container, by the addition of lead shot to the cup, until a certain outward expansion was reached, which point was indicated by the closing of an electric circuit causing a bell to ring. The weight of the shot and cup indicated the strength of the jelly. Sindall and Bacon[14] poured mercury into a glass bulb, placed upon the abraded surface of a jelly, until the bulb was forced to a half inch from the bottom, and then weighed the mercury. The Forest Products Laboratory[15] at Madison, Wisconsin, has adopted an instrument by which a weighted conical brass head is allowed to rest upon a jelly. By means of scale marked upon a frame in which the plunger slides, the depression of the plunger may be read off in millimeters. E. S. Smith[16] measured the hydrostatic pressure necessary to force a rubber diaphragm downward into a jelly a specified amount. Hulbert[17] has suggested a modification of this instrument. Low[18] has reported very satisfactory results from the use of Smith's original instrument, and regards it as more suitable for general glue work than the modification of Hulbert. C. R. Smith[19] causes a truncated cone of jelly to solidify in a funnel and then applies reduced pressure to the under surface and measures the depression of the upper surface. Sheppard and his collaborators[20] have developed an instrument by which the torsional stress of a cylinder of jelly is obtained, as well as the actual breaking load. He employs the formula

$$\frac{\text{Breaking load} \times \text{per cent twist}}{\text{Cross-section area}}$$

as the true measure of the jelly strength. This is the only truly scientific method that has yet been proposed. Oakes[21] has described the Schweizer jelly testing apparatus, which consists of a balance, in one pan of which is placed an empty beaker, and to the bottom of which is soldered a blunt plunger. These are counterpoised so that the pointers rest at zero. The jelly in a tumbler is brought into contact with the plunger, and water is allowed to run into the beaker until the pointer has reached an arbitrarily fixed deflection.

In viscosity measurements the situation is about the same. The Saybolt, Engler, and Redwood instruments have all been used. Pipet types of various designs have been described[22] and one or another of these seems in general to be most widely used. Cope[23] applied a centrifugal force to the liquid while emerging through a capillary. C. R. Smith[24] and Faust[25] have applied the "bubble method" by noting the time taken for a bubble of air of standard size to rise a given distance through the liquid. Stokes' falling sphere method has been applied recently by Sheppard,[26] Gibson and Jacobs,[27] and Fischer.[28] Flowers[29] has added the rolling sphere method to the list. Doolittle[30] described an instrument of the torsional type, an oscillating cylinder being suspended in the liquid. Garrett[31] has used a very similar device. The Couette instrument,[32] somewhat similar except that the cup containing the liquid is very slowly rotated, has been used by Hatschek[33] for exact studies on the viscosity of emulsoids. The Stormer viscosimeter has been employed by Rogers and Sabin,[34] Rigg and Carpenter,[35] and Higgins and Pitman.[36] The MacMichael instrument, described by MacMichael,[37] Herschel,[38] and Hayes and Lewis,[39] has been employed with success upon animal glues by Bogue[40] and upon casein glues by Zoller.[41]

Many methods have likewise been suggested for the melting-point determination. Chercheffski[42] measured the temperature at which small cubes of jelly became soft enough to lose their cohesion. Kissling[43] noted the temperature at which the surface of a jelly in a test tube placed horizontally became inclined. Winkelblech[44] shook a glue solution in cold water until the material had reached a consistency such that the thermometer placed vertically therein remained stationary. Küttner and Ulrich[45] describe the use of Cambon's fusiometer which consists of a metallic bowl of given dimensions and weight. A glue is allowed to gel therein, a rod being held in a vertical position in the solution. The whole is then placed in a beaker of warm water, suspended by the rod, and the temperature at which the bowl drops from the rod taken as the melting point. Herold[46] allowed a thermometer to become congealed in a test tube of glue, and noted the temperature at which the tube fell away from the thermometer when suspended in water. Sammett[47] noted the order of melting of various samples of glue when the water-swollen granules were placed on an inclined copper strip dipping in warm water. Clark and DuBois[48] determined the minimum concentration of a gelatin which would remain firm when, after making into a jelly below 10° C., the material was brought up to the temperature of 10°. C. R. Smith[49] determined the temperature at which a gelatin solution maintained a stipulated degree of viscosity, as obtained by the "bubble" method. Bogue[40] has found the viscosity at 32° to 35° C. to differentiate glues correctly according to their melting points. Sheppard and Sweet[50] have determined the temperature at which bubbles of air under a definite low pressure cease to flow through a gelatin sol.

Many other kinds of tests have also been suggested. The adhesive strength test has been used by Khars,[51] Gill,[52] Rudeloff,[53] the Forest Products Laboratory,[54] and others.[55] The tensile strength has been employed by Setherberg,[56] Gill,[52] and Hopp.[57] Optical rotation has been applied to glue testing by C. R. Smith.[19] The swelling capacity and rate of setting are occasionally mentioned as criteria for glue value.[58]

Several proposals have likewise been made for evaluating glues and gelatins by chemical means. Stelling[59] precipitates the gelatin with alcohol and determines the percentage of "nonglues" by evaporating aliquot portions of the filtrate. Precipitation of the gelatin by tannin has been used by a number of early investigators. Jean[60] used an excess of tannin and determined the excess with iodine. The value of his glues was then proportional to the amount of tannin required for precipitation. Modifications of this procedure were used by Gantter,[61] Müller,[62] Halla,[63] and Trunkel.[64] The picric acid precipitation was applied by Berrar.[65] Fahrion[66] estimated the water ash, unsaponifiable matter, fatty acids, and oxyacids, and by subtraction from 100 obtained "proteid substance." Mavrojannis[67] proposed the use of formaldehyde to separate protein and proteose from the more completely hydrolyzed peptones and amino acids. Greifenhagen, König, and Scholl[68] recommend the use of mercuric chloride and zinc sulfate. The former they claim throws down only proteoses, while the latter precipitates both protein and proteose. By difference the protein is calculated. Trotman and Hackford[69] separated the "albumoses," which included both protein and proteose, by saturating the solution with zinc sulfate. Bogue[70] has thrown down the protein with half-saturated magnesium sulfate and the protein and proteose together with the saturated salt.

This description of methods is sufficiently comprehensive to enable one to appreciate more clearly just what is signified by the statement that there is no standard procedure for the testing of glues and gelatins. In the absence of such a standard method, the diversity of tests used, as shown above, makes hopeless any attempt at an intelligent understanding of the complete significance of glue grades.

The Scientific Basis of Evaluation

Recent researches upon gelatin have brought to light many relationships that should be incorporated into the scheme of primary evaluation. From the point of view of the chemist, gelatin is a chemical compound, a pure protein, and glue is a mixture of gelatin with the products of gelatin hydrolysis, sometimes referred to as β-gelatin, and other impurities in varying amounts. Commercial gelatin and glue should, therefore, from the standpoint of *chemical constitution* be primarily evaluated in terms of the proportion of pure unhydrolyzed gelatin which is contained in the material. From the point of view of the major glue trade, *i. e.*, the use of glue as an *adhesive*, glue should be evaluated in terms of the strength of the joint, produced under the most favorable conditions, which may be made with the material. Fortunately these two points of view—that of the chemist and that of the joiner—have been shown to be identical. The glue with the largest amount of unhydrolyzed gelatin produces the strongest joint.[70]

In the primary evaluation of the material, therefore, one or the other of these two properties should be measured, or else some variable which has been found by repeated and exhaustive tests to be directly dependent upon these properties, and to express them correctly. The direct determination of either the gelatin content or the joint strength is difficult and impracticable for routine control. So the alternative procedure must be adopted. Extensive tests have been made in the author's[70] laboratory upon the relations which the jelly strength, the viscosity, and the melting point bear both to gelatin content and to joint strength, and the data obtained show clearly that if the viscosity be held constant the gelatin content and joint strength will vary as the jelly consistency, while if the latter be held constant these properties will vary as the viscosity. But the jelly consistency and the viscosity are also shown to bear the same relation to the melting point, while the latter appears to define with precision the gelatin content and the joint strength. Any method, therefore, which accurately estimates the melting point or differentiates the glues in the same order as would result from the melting point test should be a satisfactory basis for evaluation. In most glues and gelatins the viscosity and the jelly consistency are perfectly parallel functions, and a given jelly consistency will imply a definite viscosity, or vice versa, but there are many exceptions to this generality—so many in fact that were we to use either the jelly consistency or the viscosity alone as a basis of evaluation, a large number of glues would be incorrectly graded. For example, a given glue of $1^{1}/_{4}$ grade (Peter Cooper) and 22 viscosity (Alexander) may show a joining strength of, say, 2000 lbs. per sq. in. The same grade with a viscosity of 23 may show perhaps 2200 lbs. Or a grade of $1^{3}/_{8}$ and a viscosity of 22 may show 1800 lbs. Obviously, if evaluation were correctly based upon jelly consistency, the first two examples should show the same strength, and if based upon viscosity (at 60° to 80° C.), the first and third examples should be identical.

The melting point appears to be controlled by both the jelly consistency and the viscosity, and would therefore, in the cases cited, be highest in the second, intermediate in the first, and lowest in the third, which is also the order of the strength. The melting point test seems in fact to be the most readily available and practicable test as the basis for glue and gelatin evaluation.

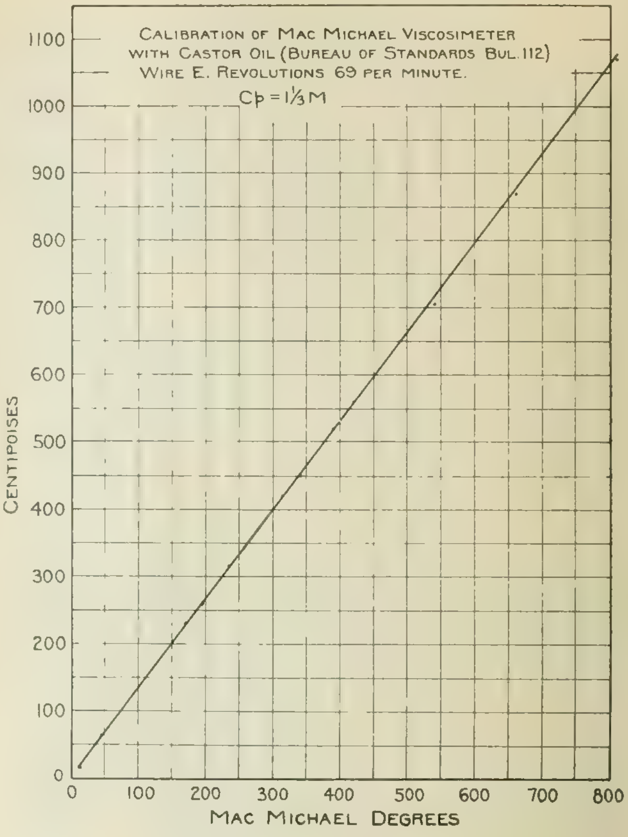
There are many methods by which the melting point may be measured, but most of these are inexact, and on account of the time required for the gel and sol forms to come to a true equilibrium, procedures intended to measure the precise temperature of melting of the jelly, or setting of the sol, are likely to be inaccurate. In an attempt to find a more rapid and accurate method for measuring this property, Bogue found that by plotting the curve of viscosity at regularly decreasing temperatures, and extrapolating to the temperature where the viscous flow would be *nil*, the figures obtained corresponded remarkably well with those obtained by several other methods of melting-point determination, both direct and indirect. But it was further observed that the same *order of differentiation* of the glues was obtained by merely taking the viscosity readings at a low temperature (32° to 35° C.). This order was, in most cases, the same as the order of viscosity at 60° C., and the order of jelly consistency at 15° C., but in all of those glues in which the viscosity was abnormal to the jelly consistency, or, vice versa, the viscosity at 32° to 35° was found to give a value intermediate between those two properties; to correspond with the true melting point; and to be precisely indicative of the gelatin content and the joint strength of the product, which was not true of any other test.*

The most satisfactory means for making this low temperature viscosity test was found to be by the use of the MacMichael viscosimeter. The advantages attendant upon the use of this instrument were found to be as follows:

1—The tests could be made very rapidly. In fact, if the glues are ready in a water bath at the proper temperature,† the viscosity tests may be made at the rate of about one per minute.

2—The instrument is a standard make, obtainable anywhere, so that its adoption would eliminate the multitudinous array of pipet and other forms of viscosimeter now in use. This would make for the standardization which is so sorely needed in glue testing practice.

3—The instrument is especially well adapted to a rapid conversion of the readings into the absolute degree of viscosity, the centipoise. The calibration of the instrument takes but a short time, and a conversion curve, which is a perfectly straight line, may be plotted, so that the MacMichael degrees may be read off in centipoises by a mere glance at the curve.‡ The centipoise unit as a standard for expressing all viscosity measurements cannot be too strongly urged. The value would be entirely independent of the size of torsion wire used, or the speed of rotation of the cup, and expresses almost exactly the specific viscosity of the material, water taken as unity, at 20 ° C.



4—Under the conditions at which the instrument would be used in glue testing, the errors, which are of considerable magnitude with many types of viscosimeter, *e. g.*, the development of turbulent flow, the increasing loss in head during the measure-

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* The temperature of 32° to 35° has been shown by C. R. Smith and by R. H. Bogue to be especially significant. Smith found this to be the temperature above which the gel form could not exist (*Loc. cit.*), and Bogue found it to be the temperature above which evidence of plastic flow could not be observed (*J. Am. Chem. Soc.*, in print).

† The glues after being soaked in the proper amount of water (see below) should be warmed to 60° C., and allowed to cool to 35° before taking the viscosity. If they are not thus preliminarily heated the readings will be erratic and unreliable, no matter how tested.

‡ The conversion curve of the instrument employed by the writer, with the use of wire number E and at a speed of 69 revolutions per minute, is shown in the accompanying figure. Castor oil was used at the advice of the Bureau of Standards, as the calibrating liquid, the absolute viscosity of which at varying temperatures is given in the U. S. Bureau of Standards *Tech. Paper* **112** (1919), 24. For the convenience of the reader, a part of the data there presented is given herewith:

ABSOLUTE VISCOSITY OF CASTOR OIL

Temperature	Viscosity in Centipoises
18	1162.5
20	986
22	834
24	706
26	604
28	521
30	451
32	394
34	340
36	294
38	258
40	231
65.6	60.5
100	16.9

Each instrument with any given wire and speed must be separately calibrated, but since the curve is a straight line, only three or four different temperature readings are required. By using wire No. 27 and adjusting to a speed of about 56.5 r. p. m., the absolute viscosity in centipoises could be read directly.

ment, inconstant and faulty drainage, the change of temperature during measurement, the abnormal values obtained when insoluble material, such as zinc oxide, is present, etc., are almost entirely eliminated. The straight line nature of the conversion curve also makes for greater accuracy in computing the absolute viscosity from the instrument reading, and by a proper adjustment of the wire and the speed of rotation the absolute viscosity in centipoises may be read directly.

A RATIONAL SYSTEM OF EVALUATION

Our discussion has shown, therefore, that the gelatin content of a glue or gelatin, and also the joint strength of a glue, may be correctly indicated by a melting-point determination, while neither may be correctly assumed to be, in all cases, proportional to either the jelly consistency or the viscosity at 60° C. alone. Inasmuch as the primary evaluation of the material should be based upon some fundamental and scientifically selected property or properties, it seems that gelatin content and joint strength should be chosen. It is especially happy that these two properties are parallel. Since the *melting point* has been shown to indicate the gelatin content and the joint strength, it seems that this determination, either directly or indirectly made, should be selected as a measure of the fundamental constitution and properties of the material. The measurement of the *viscosity of a 20 per cent solution at 32° to 35° C.* by means of the MacMichael viscosimeter has been shown to be especially well adapted as an indirect estimation of the differentiation of glues and gelatins in the order of their melting points.

Different grades of glues and gelatins normally vary in water content from about 10 to 17 per cent, the higher grades retaining the larger amount of water. Of even greater importance in evaluation is the ability of any given sample of any grade to take up or lose water according to the humidity and temperature of storage. Glues have been found to vary in water content from 9 to 18 per cent from this cause alone.

It is obvious, therefore, that a 20-g. sample may contain between 16.4 and 18.2 g. of dry glue, and since this is made, for the viscosity test, to 100 g. with water, the percentage of dry glue used in the tests will vary between 16.4 and 18.2 per cent. This is sufficient to modify very seriously the viscosity or any other test made which varies with the concentration. In order to eliminate this uncertain variable it is necessary to make a moisture determination before weighing up the samples for further tests, and it is suggested that the amount of glue to be used for the viscosity test be stipulated as the equivalent of 18 g. of dry glue made up to 100 g. with water. The temperature of 35° is probably preferable to 32° as there is less change in viscosity with time at the higher value.

If this test be accepted for the above-stated purpose, it follows that the tests for jelly consistency and for viscosity at 60° C. are no longer of service for *primary* evaluation, and may be safely discarded as such. They may, however, be of great value in *secondary* evaluation, *i. e.*, in determining the adaptability of a given glue to a given service. For example, the jelly consistency would be of value in selecting glues for printers' rollers, and the rapidity of setting of the jelly as well as the viscosity at working temperatures would be desirable data for the woodworking industry.

Another test which recent investigation has shown to be of considerable importance in determining the properties of a glue or gelatin is the *H-ion concentration.*[71] If the pH value is 4.7 the viscosity, swelling, etc., are low, and the product nearly insoluble. On either side of this point these properties increase very considerably, attaining their maximum on the acid side at $pH = 3.5$, and on the alkaline side at $pH = 9.0$. At greater acidity than $pH = 3.5$ or at greater alkalinity than $pH = 9.0$ these properties again decrease. The pH value indicates therefore not only the reaction of the material, and the degree of acidity or alkalinity, but also the proximity of the substance to the points of maximum or minimum properties. The measurement may be made by either electrometric or colorimetric means.[72] One per cent solutions are best used in either case, and the results expressed in terms of pH to the nearest tenth.

The methods that may be employed for the estimation of the secondary properties should likewise receive attention that the results may be expressed in uniform terms. The *jelly consistency* test is perhaps most conveniently made by the use of the instrument described by the Forest Products Laboratory[15] and expressed in millimeters of depression, although for some more exacting requirements, as in the selection of gelatin for photographic purposes, the more elaborate and scientific method of Sheppard[26] may be used to advantage. The *viscosity* at working temperatures, 60° C., may be made with the MacMichael viscosimeter upon an 18 per cent solution (dry basis) and the results expressed either in centipoises, or, following the suggestion of Kahrs, in pounds of dry glue which, when made up to a weight of 100 lbs. with water, will produce a solution of a given standard viscosity at 60° C. as, for example, 600 centipoises. The *foam test* may be made upon the same solution in a standard glass, by means of an egg beater turned at a stated velocity of about four revolutions per second for 30 sec., and measured after 10 sec., as millimeters of foam. The *grease test* may usually be made with sufficient satisfaction by making a streak of the glue, to which a dye such as turkey red has been added, on a sheet of paper. Better still, the glue may be mixed with the calcimine or color base with which it is intended to be used, and streaks made on paper. The *appearance* may be specified according to the information desired. The form of the product as flake, sheet, ribbon, foil, or ground, should be noted. If the glues have been treated to produce a clear light product, the degree of clarity and color should be indicated. This may usually be done with sufficient satisfaction by such terms as light, clear, medium, amber, etc., or by numerical designations as No. 1, No. 2, etc. Exact color data are best obtained by the elaborate instrument of the Eastman Kodak Company. If the glue is colored, or crazed, or presents any particular property, it should be mentioned. The *odor* should be noted in the warm solution, and a strong or sour odor should not develop, in good glues, within 48 hrs., at 30° to 40° C.

In some cases special tests will be required, as for *ash, precipitation with aluminium salts*, etc.; in the case of gelatin for edible purposes *copper, zinc, arsenic*, and *sulfur dioxide* may be determined, and in some cases qualitative tests for *preservatives* are necessary. These are made in accordance with the customary scheme for the examination of foods, as set forth in the official publications of the Association of Official Agricultural Chemists,[73] and need not be repeated here.

For the purpose of fixing an abstract valuation, or for the estimation of tariff duties on imports, the primary evaluation only need be made.

DIFFERENTIATION BETWEEN EDIBLE GELATIN AND GLUE

The methods in common use for distinguishing between edible gelatin and glue are based upon a few tests that are admittedly inadequate. The material is examined for copper, zinc, and arsenic, the maximum permissible in edible gelatin being 30, 100, and 1.4 p. p. m., respectively. The total ash is determined, the assumption being that a glue is usually higher in ash than a pure gelatin. The jelly consistency is noted, it being assumed that a glue will show much lower values for this property than gelatin. And the general appearance, color, and odor are noted, only reasonably clear and perfectly sweet gelatin being passed favorably. Sulfur dioxide is sometimes determined, but its presence is permitted in reasonable amounts. A bacteriological examination might be of value as an additional test, but many instances have been met where a gelatin gave off an offensive odor, but was found to be practically sterile. In such cases the decomposition had obviously taken place at some stage in the manufacture, but had subsequently been stopped, probably by the addition of a germicide. A periodical inspection of the care and sanitation exercised in the several steps of manufacture and in the selection of the stock used would probably be more valuable as a basis for passing upon gelatin than any chemical or other tests upon the product that could be made. Provided, however, that a gelatin passed the requirements as an edible product, then its evaluation as a gelatin should be determined primarily, as in the case of glues, upon its content of the unhydrolyzed protein, or, which has been shown to be the same, upon the melting point or viscosity at 35° C.

DESIGNATION OF GRADE

The grade designation of the product, as ascertained by the primary evaluation, may conveniently be expressed by consecutive numbers, 1 being the lowest, following the name or initial letter of the type of product. Thus hide glues may be designated as Hide Glue No. 1, Hide Glue No. 2, or H_1, H_2, and so on up to perhaps H_{15}, and bone glues as Bone Glue No. 1 or B_1, to Bone Glue No. 15 or B_{15}. If the primary evaluation is measured, as suggested, by a determination of the viscosity in centipoises of an 18 per cent solution (dry basis) at 35° C., H_1 or B_1 will correspond to a viscosity of less than 20 centipoises, and, H_{15} or B_{15} to above 150 centipoises. The arrangement might well be along the lines shown in Table III.

TABLE III—DESIGNATION OF GRADE

DESIGNATION	Viscosity of 18 Per cent Solution (Dry Basis) at 35° C., in Centipoises
H_1 or B_1	Below 20
H_2 or B_2	20 to 29
H_3 or B_3	30 to 39
H_4 or B_4	40 to 49
H_5 or B_5	50 to 59
H_6 or B_6	60 to 69
H_7 or B_7	70 to 79
H_8 or B_8	80 to 89
H_9 or B_9	90 to 99
H_{10} or B_{10}	100 to 109
H_{11} or B_{11}	110 to 119
H_{12} or B_{12}	120 to 129
H_{13} or B_{13}	130 to 139
H_{14} or B_{14}	140 to 149
H_{15} or B_{15}	150 to 159
Etc.	

Obviously the highest grades would be attained only by the very pure gelatins, while only the material that was exceedingly poor would reach the lowest designation. Both classes of glues, *i. e.*, the hide and bone types, would be rated upon the same standard, but the initial letter or name would serve the desirable purpose of differentiating between the type of stock used. Edible gelatins could be referred to, if desired, as G_{12}, G_{14}, etc., but the numerical designations should always refer to a standard viscosity or other value fixed as the primary standard for evaluation.

The laboratory test sheet would appear about as indicated in Table IV.

ADVANTAGES OF PROPOSED SYSTEM

The advantages of such a system, or of any other that secures a real standardization based upon fundamental and scientific principles, are strikingly apparent. Where the jelly consistency is taken as the basis of determining grade, a set of "standard" glues must be maintained, and in the course of a few years these standard types, through occasional renewal, must inevitably alter. Furthermore, the curves for the jelly consistency of various glues at varying temperatures are not parallel, but a glue that is weaker than the standard at 10° may be the stronger at 15°. There is surely no good reason why the tests should be made at one temperature in preference to any other, but the decision upon this very arbitrary point determines the rating which a glue may receive by the current methods.

Mention has already been made of the diversity of instruments used in making the viscosity test, and the impossibility, without profound instrumental corrections, of expressing the readings obtained in terms of absolute viscosity, or any other kind of viscosity that will be intelligible to a person using any other instrument.

And most important of all, the figures obtained by the jelly strength and the high-temperature viscosity methods do not give data which are invariably expressive of any fundamental property.

These objections the proposed changes seek to remedy. The primary evaluation involves the use of no arbitrarily selected "standard" glues, but gives results that are in themselves complete without reference to any other hypothetical product. The use of a standard instrument which readily permits the employment of absolute degrees enables the readings to be understood universally, and the data obtained are indicative of fundamental properties of the material.

The grade designated is simple and very easily understood. The letter referring directly to the type of stock, and the number to the absolute viscosity, reduces to the vanishing point any mystery connected with glue grades, and enables the layman to define a glue with nearly the same degree of intelligence as may be exercised by the expert.

BIBLIOGRAPHY

1—*Bur. Chem., Bull.* **109**, revised (1910), 54.

2—R. L. Fernbach, "Glues and Gelatine," New York, **1907, 4**.

3—J. Alexander, *J. Soc. Chem. Ind.*, **25** (1906), 158.

4—F. Kahrs, International Fisheries' Congress, Bergen, Norway, **1898**.

5—L. A. Thiele, Personal communication.

6—J. Fels, *Chem.-Ztg.*, **21** (1897), 56; **25** (1901), 23.

7—V. L. Cerri, Report to Italian Military Aviation Board, **1920**.

8—E. G. Clayton, *J. Soc. Chem. Ind.*, **21** (1902), 670.

9—R. L. Fernbach, *Loc. cit.*, **47**.

10—Lipowitz, "Neue Chemische Technologische Untersuchungen," Berlin, **1861**, 37.

11—R. Kissling, *Chem.-Ztg.*, **17** (1893), 726; **22** (1898), 171.

12—Valenta, *Ibid.*, **33** (1909), 94.

13—Scott, *Chem. Eng.*, **5** (1907), 441.

14—Sindall and Bacon, *Analyst*, **39** (1914), 20.

15—*Forest Products Lab. Tech. Notes*, **F 32** (1919).

16—E. S. Smith, U. S. Patent 911,277, February 2, 1909.

17—E. Hulbert, *J. Ind. Eng. Chem.*, **5** (1913), 235.

18—W. H. Low, *Ibid.*, **12** (1920), 355.

19—C. R. Smith, *Ibid.*, **12** (1920), 878.

20—Sheppard, Sweet and Scott, *Ibid.*, **12** (1920), 1007.

21—E. T. Oakes, 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

TABLE IV—GLUE AND GELATIN TEST SHEET

LOT——————

DATE——————

PHYSICAL TESTS									CHEMICAL TESTS						
DESIGNATION No.	DESIGNATION Grade	Viscosity in Centipoises at 35° C. 18 Per cent Soln.	pH 1 Per cent Soln.	Jelly Consistency Mm. Depression 10° C. 18 Per cent Soln.	Foam Mm. 18 Per cent Soln.	Grease	Appearance	Odor	Moisture Per cent	Ash Per cent	Copper P. p. m.	Zinc P. p. m.	Arsenic P. p. m.	Sulfur Dioxide Per cent	REMARKS Special Tests
49440	H_7	72	5.7	4.2	14	....	Dark, flake	Sweet	12.7	....	..	...	...	....	....
50214	H_4	46	6.9	8.1	28	....	Brown, flake	Sour	11.0	....	..	...	...	....	....
46621	B_9	90	3.7	4.1	..	....	No. 1 Sheet	Sweet	14.2	....	..	...	...	....	No. ppt. with alum
46602	B_1	17	4.9	Liquid	8	Present	Crazed, flake	Strong	10.4	....	..	...	...	....	....
80441	G_{13}	130	6.8	2.1	10	Absent	Light, ground	Sweet	16.2	1.82	10	20	0.0	.0102	O. K.
50266	B_7	78	5.4	...	13	....	White, flake	Sweet	12.2	8.7	..	...	...	....	....
70222	G_{15}	156	7.1	1.2	..	Absent	Amber, ground	Sweet	17.3	3.31	10	220	7	.027	Technical only

Performed by——————

Approved by——————
Chemist

22—J. Fels, *Loc. cit.;* F. Kahrs, "Glue Handling," East Haddam, Conn., **1905-6**, 58; R. Fernbach, *Loc. cit.*, 38; J. Alexander, *Loc. cit.;* National Advisory Committee on Aeronautics, *Report* **66** (1920), 26.

23—W. C. Cope, *J. Ind. Eng. Chem.*, **9** (1917), 1046.

24—C. R. Smith, *J. Am. Chem. Soc.*, **41** (1919), 135.

25—O. Faust, *Z. physik. Chem.*, **93** (1919), 758.

26—S. E. Sheppard, *J. Ind. Eng. Chem.*, **9** (1917), 523.

27—Gibson and Jacobs, *J. Chem. Soc.*, **117** (1920), 473.

28—R. Fischer, *Chem.-Ztg.*, **44** (1920), 622.

29—A. E. Fellows, *Proc. Am. Soc. Test. Materials*, **14** (1914), 565.

30—Doolittle, *J. Am. Chem. Soc.*, **15** (1893), 173.

31—Garrett, *Phil. Mag.*, [6] **6** (1903), 374.

32—Couette, *J. phys.*, **9** (1890), 414; *Ann. chim. phys.*, **6** (1890), 21, 502.

33—E. Hatschek, *Trans. Faraday Soc.*, **9** (1913), 80.

34—A. Rogers and A. Sabin, *J. Ind. Eng. Chem.*, **3** (1911), 737.

35—G. Rigg and J. Carpenter, *Ibid.*, **4** (1912), 901.

36—E. Higgins and E. Pitman, *Ibid.*, **12** (1920), 587.

37—R. MacMichael, *Ibid.*, **7** (1915), 961.

38—W. H. Herschel, *Ibid.*, **12** (1920), 282.

39—Hayes and Lewis, *J. Am. Soc. Mech. Eng.*, **38** (1916), 626, 1002.

40—R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 61, 197.

41—H. F. Zoller, *J. Ind. Eng. Chem.*, **12** (1920), 1171; *J. Gen. Physiol.*, **3** (1921), 635.

42—Chercheffski, *Chem.-Ztg.*, **25** (1901), 413.

43—Kissling, *Z. angew. Chem.*, **16** (1903), 398.

44—Winkelblech, *Ibid.*, **19** (1906), 1260.

45—Küttner and Ulrich, *Z. öffentl. Chem.*, **13** (1907), 121.

46—Herold, *Chem.-Ztg.*, **34** (1910), 203.

47—C. F. Sammet, *J. Ind. Eng. Chem.*, **10** (1918), 595.

48—A. Clark and L. DuBois, *Ibid.*, **10** (1918), 707.

49—C. R. Smith, *J. Am. Chem. Soc.*, **41** (1919), 146.

50—S. E. Sheppard and S. Sweet, *J. Ind. Eng. Chem.*, **13** (1921), 423.

51—F. Khars, *Glue*, **1** (1910), No. 3, 4; No. 4, 5; No. 5, 8; No. 6, 10.

52—A. H. Gill, *J. Ind. Eng. Chem.*, **7** (1915), 102.

53—M. Rudeloff, *Mitt. kgl. Materialprüfungsamt*, **36** (1918), 2; **37** (1919), 33.

54—National Advisory Committee for Aeronautics, *Report* **66** (1920), 21.

55—See A. Heineman, *Chem.-Ztg.*, **24** (1900), 871; J. Welmers, *Veneers*, **14** (1920), 35; R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 197.

56—Setterberg, *Schwed. Tech. Tidskrift*, **28**, 52.

57—G. Hopp, *J. Ind. Eng. Chem.*, **12** (1920), 356.

58—See Shattermann, *Dinglers polytech. J.*, **96** (1845), 115; Reardon, "Something about Glue," **1910**.

59—C. Stelling, *Chem.-Ztg.*, **20** (1896), 461,

60—F. Jean, *Ann. chim. anal.*, **2** (1897), 85.

61—F. Gantter, *Z. anal. Chem.*, **32** (1893), 413.

62—A. Müller, *Z. angew. Chem.*, **15** (1902), 482.

63—Halla, *Ibid.*, **20** (1907), 24.

64—Trunkel, *Biochem. Z.*, **26** (1910), 458.

65—Berrar, *Ibid.*, **47** (1912), 189.

66—Fahrion, *Z. angew. Chem.*, **8** (1895), 529.

67—Mavrojannis, *Z. Hyg.*, **45** (1904), 108.

68—Greifenhagen, König and Scholl, *Biochem. Z.*, **35** (1911), 217.

69—S. Trotman and J. Hackford, *J. Soc. Chem. Ind.*, **23** (1904), 1072.

70—R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 105, 154.

71—See J. Loeb, *J. Gen. Physiol.*, **1** (1918–19), 39, 237, 363, 483, 559; **3** (1920–21), 85, 247, 391; R. H. Bogue, *J. Am. Chem. Soc.*, **43** (1921), 1764.

72—See W. M. Clark, "The Determination of Hydrogen Ions," Baltimore, **1920**.

73—Assoc. Official Agr. Chem., "Methods of Analysis," 2nd edition, **1920**, 147.

Potash from Kelp[1,2]

VI—The Decolorizing Action of Adsorptive Charcoals

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The theory that the decolorizing action of charcoals is due primarily to the presence of an organic nitrogenous compound in charcoal is not upheld. On the other hand, the impurities in a charcoal are frequently responsible for many peculiar effects usually ascribed to "charcoal."

The adsorption theory of dyeing is reviewed briefly, and applied to the decolorization of sugar sirups and cottonseed oil by charcoal.

THE extreme difficulty of preparing a charcoal[3] absolutely free from oxygen, hydrogen, nitrogen, and other impurities perhaps led to the belief that these impurities were essential to give charcoal the property of decolorizing various solutions.[4] Patterson[5] was one of the early advocates of such a theory, and his work has had acceptance even up to the present.[6] It has been suggested recently by Bancroft[7] that Patterson's work be repeated. This has been done by Hall[8] who confirmed Patterson's results. The latter isolated an organic nitrogenous material of gelatinous nature from boneblack, and claimed that this substance was chiefly responsible for the decolorizing action of bone char. He calculated that this nitrogenous compound was from sixteen to forty times as active a decolorizer as the original char. The fact that wood charcoals contain practically no nitrogenous substance and have very little decolorizing power he took as further evidence in support of his theory.

Recently a number of charcoals of vegetable origin, including kelpchar, the decolorizing carbon manufactured from the Pacific Coast kelp,[9] *Macrocistis pyrifera,* have been prepared which have many times the decolorizing efficiency of bone char, and yet do not contain this supposedly essential nitrogenous constituent. The argument might be advanced, however, that these charcoals possessed superior activity in spite of this fact.

One of the objectives at this Laboratory was to activate kelpchar as highly as possible, and as a part of this investigation it was necessary to determine just how important it was to have present Patterson's nitrogenous compound.

Patterson isolated the compound by treating 1 g. of purified boneblack first with a few cc. of cold concentrated sulfuric acid. The acid dissolved a substance which imparted a brown color to the solution. After separating the acid from the residue and diluting it with 10 to 12 volumes of water, a gelatinous precipitate was formed which settled with difficulty. The char was treated with a second and a third portion of acid, these times the acid being hot. In each instance a brown gelatinous precipitate was produced on dilution of the acid. If the acid became too dilute as a result of attempts to wash the precipitate, the latter would not settle. Patterson added the acid suspension to a caramel solution and diluted to a definite volume. When the precipitate settled he compared the supernatant liquid colori-

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[1] Received January 4, 1922.

[2] Published with the permission of the Secretary of the Department of Agriculture.

[3] Bancroft, *J. Phys. Chem.*, **24** (1920), 127, 201, 342.

[4] Glassner and Suidu, *Ann.*, **361** (1908), 351; Knecht and Hibbert, *J. Soc. Dyers Colourists*, **32** (1916), 226.

[5] *J. Soc. Chem. Ind.*, **16** (1903), 608.

[6] C. F. Bardorf, *Facts about Sugar*, **11** (1920), 351; W. D. Horne, *Ibid.*, **11** (1920), 372.

[7] THIS JOURNAL, **13** (1921), 155.

[8] *Ibid.*, **14** (1922), 18.

[9] THIS JOURNAL, **10** (1918), 812; **11** (1919), 864.

metrically with a standard caramel solution of equal dilution. The decrease in color in one instance amounted to 33.3 per cent and in another to 42.4 per cent. The precipitated organic matter in the first experiment was 0.0198 g. and in the second 0.010 g. Since an equal volume of diluted caramel solution would be completely decolorized by 0.9542 g. of boneblack, Patterson calculated the organic constituent of boneblack to be from 16.03 to 40.46 times better as a decolorizer than the char itself.

The refinement of these calculations would infer a much greater degree of precision in experimental work than would seem to be justified by the wide difference in the two results. Patterson excuses this disagreement by pointing out that the extractions were made at different temperatures, and that different bodies were extracted which had decolorizing characteristics peculiar to themselves. Another explanation of his results is given below.

Decolorizing Action of Acid

It will be noticed that Patterson made no attempt whatever to duplicate conditions regarding acidity when comparing the decolorizing efficiencies of boneblack and the several gelatinous suspensions. Such a precaution is very necessary, as was pointed out in a previous paper,[10] and the neglect of this precaution may possibly explain the apparently anomalous behavior of charcoal in different solutions, as well as the extravagant claims of some charcoal patentees of to-day. It was suspected that the remarkable decolorizing power of Patterson's suspensions was due, not to the few milligrams of the solid material, but to the acid in which they were suspended. This supposition was confirmed by the following test:

A neutral caramel solution was prepared of a concentration such that 1 cc., after being diluted to 100 cc., would be decolorized by 1 g. of the best decolorizing boneblack on hand. A quantity of this weaker standard solution was made up, and to 100 cc. of it was added one drop of concentrated sulfuric acid. Comparison with the original solution showed that the acid had caused a decrease in color amounting to 25 per cent. More acid caused more color to disappear, although the solution did not become colorless even with considerable excess acid.

These facts afford a much simpler explanation of Patterson's results and easily account for the wide divergence in decolorizing values of his suspensions, it being highly improbable that the same amount of acid was added to the caramel solution in each instance.

Patterson did not show that the decolorizing property of charcoal was diminished by the removal of the organic body. He may have attempted to do this and failed, as did the present writer, because concentrated sulfuric acid so altered the form and character of the char that strictly comparable results with the initial and final char could not be made.

The view that acid caused the decolorization of the caramel solution and not the gelatinous precipitate receives further support from Patterson's own observations: that the precipitate suspended in acid was a good decolorizer, whereas the dried precipitate possessed practically no decolorizing power.

It is not intended that these remarks should support the view that the impurities in a charcoal have no influence on the decolorizing action, as quite the contrary is usually true. What is desired is to emphasize that charcoal is a complex substance, and that the impurities in it may or may not play an important role when a charcoal (or gelatinous precipitate) decolorizes a solution. Sometimes these impurities act adversely, and sometimes coöperatively with a charcoal. On some occasions they may be without influence at all.

Thus, if salts or oxides of iron be present in a charcoal, and such a charcoal be added to an unbleached citric acid solution, the iron will react with some of the impurities of the solution and form very highly colored compounds. Although the charcoal adsorbs a portion of these compounds, the amount left behind may be so highly colored that the solution appears more colored than the original.

Further, a charcoal may contain free acid. Then on being added to neutral sugar sirup, a greater decolorization will be produced than if the charcoal had been neutral or alkaline.

The acid in this instance acts along three lines. In the first place, there are substances in cane sugar sirups which act like indicators, being less colored in the presence of acid than in alkali. The second effect of the acid is to lower the solubility of the color-forming compounds, thus making it easier for the charcoal to adsorb them. That such compounds exist in cane sugar sirups was shown by Zerban[11] who isolated a group of polyphenols and showed that these compounds caused much of the color of the sirup. These phenols are acidic in nature; therefore if strong acid were added to the solution their ionization would be repressed. This would cause diminished color intensity and solubility. The lessened solubility[12] would allow them to be more readily adsorbed by charcoal.

The third effect of acid is to furnish H ions for the charcoal to adsorb. H ions and OH ions are especially adsorbed by charcoal.[13] The adsorption of H ions causes the charcoal to become positively charged, and since the color radical of the phenol is negatively charged, the mutual attraction causes the solution to be decolorized.

Hydroxyl ions, having the reverse effect, make possible the use of alkali for regenerating spent "sugar charcoal."

Adsorption Theory of Dyeing

The extraordinary importance which H ions and OH ions play in the decolorization of liquids by charcoal led to the conclusion that the phenomenon was the same as that exhibited by a fabric when removing dye from a dye bath. The impurities in a solution to be decolorized or deodorized are the dyes, and the charcoal is the fiber. That charcoal will act like a piece of cloth in removing dye from solution is not new to dye chemists,[14] but the application of this knowledge to the decolorization of sugar sirups and other solutions seems to have been entirely overlooked. Industrially, charcoal is applied in a most empirical manner. Much assistance could be had in setting the correct conditions for the most efficient usage of charcoal if some of the generalities of dyeing be kept in mind.

Bancroft[15] states that:

> A fiber tends to adsorb everything in solution in amounts varying with the nature, concentration, and temperature of the solution, and the nature of the fiber. * * * * A basic dye is one which contains the color in the basic radical, while an acid dye contains the color in the acid radical. * * * * In order to get the maximum adsorption of an acid dye, we should have present an ion of the opposite charge, which is readily adsorbed. In case of basic dyes, the dye should be more readily taken up in a neutral or alkaline solution. Acids (hydrogen ions) decrease the dyeing of basic dyes and increase that of acid dyes. This action is proportional to the concentration of hydrogen ions. Bases (hydroxyl ions) have just the opposite effect.

When wool is dipped in an acid dye solution such as picric acid, the quantity of dye removed will be greater the higher the H-ion concentration. If wool be made to adsorb a basic dye, such as malachite green, H ions inhibit the color removal and OH ions increase it. In this connection it might be worth while to mention that some laboratories prefer to compare charcoals by observing the decolorization produced on a dye solution such as malachite green. The importance of having identical concentrations of H ions or OH ions throughout a series of tests will now be apparent.

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[10] This Journal, **14** (1922), 19.

[11] This Journal, **11** (1919), 1034.

[12] Lundelius, *Kolloid Z.*, **26** (1920), 145.

[13] Rona and Michaelis, *Biochem. Z.*, **94** (1919), 240.

[14] Pelet-Jolivet, "Die Theorie des Farbeprossess," **1910**, 58.

[15] *J. Phys. Chem.*, **18** (1914), 1.

In a qualitative way the effect of acid and alkali on the decolorization of sugar sirups has already been described. Bradley[16] quantitatively studied the effect of acidity on the decolorization of sugar molasses and found that the decolorization was nearly proportional to the quantity of acid present. This agrees well with the above-outlined theory. He was surprised, however, to find that when equivalent quantities of both weak and strong acids were used the decolorization was nearly equal in each case. Citric or tartaric acid was just as effective as sulfuric acid. In the interpretation of these data it should be remembered that an acid is made up of two parts, and that each ion influences the equilibrium independently. Therefore, when decolorization tests are made with different acids, the result in each case will be the net result produced by the H ions and the corresponding acid ions. When citric acid is compared with hydrochloric acid, the citrate ions and chloride ions affect the equilibrium as well as the H ions. The weaker concentration of H ions afforded by the citric acid tends to cause less color to be removed than by an equivalent amount of hydrochloric acid. On the other hand, the coagulating effect of the citrate ion on the sugar colloids is much greater than that of the chloride ion. The net result of these two acids may thus be about the same.

By increasing the concentration of sugar in a molasses solution Bradley found the decolorizing efficiency to be reduced. This is not surprising when one accepts the view that adsorption is a matter of equilibrium, and that this equilibrium depends upon the nature and concentration of everything in solution. The colors are evidently more soluble in the concentrated sugar solution and therefore adsorbed to a lesser extent.

The above theory regarding the decolorization of liquids with charcoal, although based principally upon experiments made with aqueous solutions, has promise of extension to nonaqueous solutions. This is a relatively new field for charcoal and facts are none too numerous.

Cottonseed oil contains some colored impurities which on electrolysis migrate toward the negative pole. These particles are therefore positively charged and may be considered as basic dyes. Accordingly, if OH ions, or for that matter any other negatively charged ions readily adsorbed by charcoal in cottonseed oil, were added to the oil along with the charcoal, color removal should be increased. If the solution were acid, which would allow H ions to be adsorbed, removal of color would be hindered.

The latter may be demonstrated by adding a little glacial acetic acid to the oil before adding the charcoal. The acid has no apparent physical or chemical effect on the oil, but distinctly reduces the decolorizing effect of the charcoal.

It would be of interest in this connection to note the action of some material soluble in cottonseed oil, which would furnish a negative ion readily adsorbed by the charcoal. Such a condition should promote the removal of color. Direct evidence on this point is lacking, but there is a certain analogy between the action of fuller's earth and what would be expected to happen were charcoal given a negative charge. According to Glick,[17] fuller's earth becomes negatively charged when placed in cottonseed oil, and this property enables it to remove the positive colors.

Fuller's earth[18] probably owes its negative charge to the OH or other negative ions which it adsorbs strongly. The positive colors are literally dragged along and attached to the earth because of electrostatic attraction—an action similar to that of charcoal, H ions, and negative colors.

Charcoal does not show this preferential adsorption of OH ions; it adsorbs OH or H ions with equal avidity.[18] These facts are useful in explaining why fuller's earth has been used chiefly for oil purification and not for sugar, and why charcoal, except recently, has been used for sugar sirups and not oils.[19]

Suppose fuller's earth be placed in sugar sirup. If the solution be neutral or alkaline, the earth will adsorb OH ions and repel most of the color ions. If the solution be acid practically no ions will be adsorbed. On the other hand, when charcoal, comparable in activity with fuller's earth, is placed in alkaline sugar sirup, OH ions will be adsorbed, but less so than in the case with fuller's earth. There is, therefore, less repellent action on the phenols and somewhat more decolorization. The action in acid solution has already been described.

This preferential adsorption by fuller's earth of basic dyes is at least one reason why in the past it has been used instead of charcoal for oil purification. Recently charcoals such as kelpchar have been prepared whose adsorptive intensity and capacity (activity) for all ions, both positive and negative, have been so increased as to overlap the region occupied by fuller's earth. These charcoals are now being used to some extent for oil purification. Whether or not fuller's earth or materials of similar nature will have their adsorptive characteristics so developed as to compete with or displace these newer charcoals is a question for the future to decide.

In harmony with the "dye" theory of decolorizing solutions is a fact brought out by Glick that with some oils a mixture of earth and charcoal is more effective than either alone. In such a mixture the earth may be considered to be adsorbed by the charcoal, and to give the charcoal a greater negative charge than the latter could possess by itself. The additional charge allows the charcoal to make fuller use of its great surface and produces greater decolorization. Steric hindrance probably prevents the earth from utilizing its charge completely when used alone. In the language of the dye chemist, charcoal might be said to have been "mordanted" with fuller's earth. If this explanation be true it points to many interesting developments. Charcoal in the future may be expected to be mordanted with materials that will direct its action along specific lines, just as cotton is mordanted according to the dye it is expected to take up.

Just as the nature of a fiber affects the equilibrium in a dye bath, so the nature of a charcoal affects the decolorization of a solution. Charcoals differ because of the variety of raw materials from which they are derived, and because of the divers methods used in manufacture. Some charcoals will be characterized by relatively shallow capillaries, others will have longer ones.[20] The total surface area per gram of material will be different, also the number and position of "elementary spaces."[21] Steric hindrance[22] will frequently be a determining factor. The instantaneous[23] or pseudo-equilibrium as well as the final equilibrium will vary with the charcoal.

Although physical structure plays an important part in the behavior of a charcoal, its position must not be overemphasized. There are other factors just as important as, and probably more so than "cellular structure." As an example of this, a charcoal was prepared from kelp juice that had identical decolorizing characteristics of charcoal made from the body of kelp itself. Also, as a decolorizer, blood charcoal is far more powerful than many other charcoals made from materials of a more definite structure. In studying charcoal, therefore, it is well to keep in mind that it is a complex substance and that the results seldom depend upon any one characteristic.

[16] *J. Soc. Chem. Ind.*, **39** (1919), 396.

[17] *Cotton Oil Press,* **4** (1921), 41.

[18] Cameron, *J. Phys. Chem.*, **14** (1910), 400.

[19] Sneller, *Louisiana Planter*, **59** (1917), 154.

[20] Dorsey, THIS JOURNAL, **11** (1919), 383.

[21] Langmuir, *J. Am. Chem. Soc.*, **40** (1918), 1361.

[22] Langmuir, *Ibid.*, **38** (1916), 2221; **39** (1917), 1848.

[23] McBain, *Trans. Faraday Soc.*, **14** (1919), 201; Cude and Hulett, *J. Am. Chem. Soc.*, **42** (1920), 391; Bradley, *Loc. cit.*; Lamb, Wilson and Chaney, THIS JOURNAL, **11** (1919), 420; Sheldon, *Proc. Nat. Acad. Sci.*, **6** (1920), 178; Lemon, *Ibid.*, **5** (1919), 291.

First Report of the Committee on Contact Catalysis

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(Continued)

Promoter action is by no means confined to the ammonia synthesis. Pease and Taylor[44] have collected the data on promoter action. Ipatiew[45] found that copper oxide in an iron tube was much more effective in causing the hydrogenation of amylene than was copper oxide in a copper tube. The Badische Company[46] state that hydrogenation of fats with nickel is accelerated by the presence of tellurium. Dewar and Liebmann[47] claim that a mixture of nickel and copper oxides can be reduced in the oil at 190° and will hydrogenate cottonseed oil rapidly at that temperature, whereas nickel oxide alone requires a temperature of about 250° for reduction. Hochstetter[48] found that a mixture of silver and copper was more effective for the synthesis of formaldehyde from methanol than either metal singly. Maxted[49] states that bismuth, tungsten, and copper make iron more active in the ammonia oxidation. Mixed oxides are more effective in the oxidation of carbon monoxide than any of the oxides taken singly. The phenomenon of promoter action is thus a fairly common one.

ORIENTED ADSORPTION

Though Langmuir considers adsorbed substances as held by bonds or contravalences to the adsorbing agent and though he speaks of oriented adsorption, he has never gone into details in regard to this and it is by no means certain that his conception of oriented adsorption is the same as that of an organic chemist, for instance. For the moment it looks as though the organic chemist were the safer man to follow. The immediate problem is to devise methods of telling what particular bonds or contravalences are effective in causing the adsorption of ethyl acetate, for instance, by any given catalytic agent. Having done that we must show that the opening up of those particular bonds or contravalences are the necessary prerequisite to the reaction which is produced by that particular catalytic agent. When this has been done, the next problem will be to develop a theory which will enable us to predict that a given catalytic agent will cause such and such bonds or contravalences to open; but that lies quite a way in the future. It must also be remembered that, for the other type of contact catalysis, the identification of the intermediate compounds does not account for the catalytic action. On the other hand, it is impossible to take the next step until the intermediate compounds have been identified.

If we adopt the hypothesis that part, at any rate, of the catalytic action of a given adsorbent is due to oriented adsorption, it is clear that we may have an adsorbent slowing down the reaction in case the orientation is unsatisfactory. This seems to have been realized by Kruyt and van Duin.[50] They find that the following reactions are retarded by charcoal although the reacting substances are adsorbed by it: the saponification of ethyl acetate and of sodium methyl-benzoate-*p*-sulfonate; the addition of bromine to the acid sodium salt of *p*-sulfo-cinnamic acid; the removal of bromine from the neutral and the acid sodium salts of *p*-sulfonic-dibromohydrocinnamic acid by means of potassium iodide. On the other hand, the removal of bromine from α,β-dibromopropionic acid by means of potassium iodide is accelerated by the presence of charcoal.

The authors conclude from these results that adsorption involves more than a mere increase of concentration at the surface.

> This conclusion is quite in harmony with the theories of Langmuir,[51] and Harkins[52] and his collaborators. In addition to a surface concentration there is also an orientation. This latter may cause a decrease in the reaction velocity. If the two adsorbed, reacting substances are not free in their movements, their chances of encountering one another are decreased, and the probability that they will get into a state favorable to the reaction may be changed for the worse.
>
> There is yet another reason why the reaction may be checked. At the surface between water and a phase consisting of carbon or of carbon compounds, the molecules will turn their more polar portion towards the water. If the reaction takes place at a nonpolar, or less polar, portion of the molecule, this part is turned away from the aqueous phase and from the substances dissolved in it. If the two reacting substances are more or less polar, it may be that they will be adsorbed in such a way that the reacting portions are turned away from each other. From this point of view, it is clear why we obtained a negative catalysis at first in spite of the adsorption. It is true that the aromatic substances are adsorbed strongly; but in order to make them soluble we had introduced the radical SO_3Na. This radical increases the solubility very much and is also highly polar.
>
> We can therefore form the following conception as to the position taken by the molecules at the surface between the charcoal and the liquid. In the acid sodium salt of *p*-sulfocinnamic acid we have the following arrangement.[53] The benzene ring with three double bonds tends to place itself horizontally on the surface; but this is interfered with by the polar groups in the para position. In view of the strongly acid character of the sulfonic acids and especially in view of their effect in increasing the solubility, the radical SO_3Na is undoubtedly more polar than the radical $CH:CH.CO_2H$. The first tends to draw the portion of the benzene ring to which it is attached into the water, which means that the other is pushed toward the charcoal. It is, however, this unsaturated side chain which reacts with the bromine. In the case of sodium methyl-benzoate-*p*-sulfonate, the organic side chain is in a disadvantageous position. The small molecules of adsorbed bromine or caustic soda (or perhaps the free sodium and hydroxyl ions) will undoubtedly all be at the water surface and will find turned from them the radicals with which they should react.[54] The dissolved and unadsorbed molecules of bromine and of sodium hydroxide are handicapped in the same way. In spite of the increased concentrations the conditions at the surface of the adsorbent are unfavorable to the progress of the reaction and out in the solution the reaction goes more slowly because of the decreased concentrations there in consequence of adsorption.
>
> The situation is undoubtedly as follows in the case of ethyl acetate. In the molecule $CH_3CO.C_2H_5$ the radical $C:O$ is unquestionably the most polar and it is probably the doubly tied oxygen which sticks out into the water and the ethoxy group OC_2H_5 is consequently more or less buried.
>
> We tried at first to increase the polar character of the cinnamic acid radical. The acid sodium salt of the *p*-sulfonic-dibromohydrocinnamic acid is more soluble in water than the corresponding compound containing no bromine, and since the bromine increases the solubility of the compound it must increase the polarity of the group. The remarkable reaction of the bromine addition compound with potassium iodide made it seem probable that the bromine atoms had brought the side chain out enough to make it react with the potassium iodide in solution.[55]

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[44] *J. Phys. Chem.*, **24** (1920), 241.

[45] *Ber.*, **43** (1910), 3387.

[46] D. R. P. 282,782 (1913).

[47] U. S. Patents 1,268,692; 1,275,405.

[48] U. S. Patents 1,100,076; 1,110,289.

[49] *J. Soc. Chem. Ind.*, **36** (1917), 777.

[50] *Rec. trav. chim.*, [4] **2** (1921), 249.

[51] *J. Am. Chem. Soc.*, **38** (1916), 2221; **39** (1917), 1848.

[52] *Ibid.*, **39** (1917), 354, 541.

[53] Harkins, Davies and Clark, *Ibid.*, **39** (1917), 582.

[54] [Since bromine is much more soluble in organic liquids than in water, this does not necessarily follow.]

[55] [Since potassium iodide is adsorbed strongly by charcoal, the reaction may be with the adsorbed iodide and not with the dissolved iodide.]

> In order to make doubly sure, the radical COOH was converted into COONa. Since the results were negative we concluded that the polar effect of SO_3Na was still preponderant. * * *
>
> Since it was difficult to avoid the radical SO_3Na in reactions with aromatic compounds in aqueous solutions and since its polar character often turns the scale, we tried to find some other method of escaping from this dilemma. According to Harkins we should have better prospects of success if we selected a suitable aliphatic compound. The criteria seemed to be met by the α,β-dibromopropionic acid. There is a polar effect at each one of the three carbon atoms and, according to the theory of Harkins, the chain of carbon atoms should seek a position parallel to the boundary surface, so that the three polar groups would turn to the water. It was possible of course that one of the groups, COOH or Br, would be the more powerful and would make the carbon chain asymmetric; but, even so, the conditions were much more favorable than in the preceding experiments with sulfonated aromatic compounds. As a matter of fact, charcoal does accelerate the reaction.

POISONS

While we are still very much at sea as to any satisfactory theory of contact catalysis, matters are in much better shape in regard to what was at one time a most mysterious phenomenon—the poisoning of the catalytic agent. On any theory of contact catalysis except radiation at a distance, the reaction takes place in or at the surface of the catalytic agent. A necessary consequence of this is that any substance, which cuts down the rate at which the reacting substances reach the catalytic surface[56] or which prevents them from reaching it,[57] will decrease the reaction velocity and may destroy the catalytic action entirely. Berliner[58] has shown that traces of fatty vapors from the air or from the grease on the stopcocks will decrease the adsorption of hydrogen by palladium from about nine hundred volumes to nothing. Pollard has observed a similar decrease with platinized asbestos from about one hundred and forty volumes to a negligible amount. Faraday[59] proved that traces of grease destroy the catalytic action of platinum black. Lunge and Harbeck[60] found that carbon monoxide inhibits practically completely the catalytic action of platinum on a mixture of ethylene and hydrogen. Taylor and Burns[61] conclude from their experiments that "even when pressures of carbon monoxide not exceeding a few centimeters exist, it is reasonable to suppose that the platinum surface remains covered so thoroughly with carbon monoxide that hydrogen or other gases are unable to reach it." They also point out that platinum which holds carbon monoxide so tenaciously is not a good catalytic agent for the reduction of carbon monoxide to methane, whereas this reaction takes place readily with palladium from which carbon monoxide can be removed readily by hydrogen at ordinary temperatures.

Schönbein[62] pointed out that the hydrides of sulfur, tellurium, selenium, phosphorus, arsenic, and antimony act very energetically in cutting down the action of platinum on mixtures of air with hydrogen or ether. Since he did not realize that an adsorbed gas film might keep out other gases, he decided that the hydrides must decompose, giving rise to a solid film. This hypothesis is not necessary to account for the phenomenon; but he was right in at least one case, for Maxted[63] has found that hydrogen sulfide is decomposed by platinum black with evolution of hydrogen and that the sulfurized platinum does not adsorb hydrogen. Maxted[64] has also studied the poisoning action of lead on platinum. The effect is apparently proportional to the amount of lead, 1 mg. of lead neutralizing or paralyzing 8.8 mg. of platinum. Paal and Steger[65] have shown that mercury displaces hydrogen from a palladium hydrosol. Langmuir[66] believes that oxygen prevents the dissociation of hydrogen by a heated tungsten filament because it cuts down the adsorption of the hydrogen. He states that:

> The action of oxygen preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a catalytic poison. It has been shown previously[67] that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the surface of the tungsten. The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface. Since the dissociation at 1500° K. is entirely prevented by the oxygen, and since the range of atomic and molecular forces does not exceed the dimensions of the atoms, it must follow that much more than half the surface must be covered by oxygen atoms or molecules. For if the surface were only half covered, then, according to probability laws, uncovered areas several times as large as the diameters of atoms would not be of rare occurrence, and on these areas dissociation could occur.

Harned[68] has shown that the rate of adsorption of chloropicrin by a charcoal which has been cleaned by washing with chloropicrin is much greater at first than by a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. This is analogous to the evaporation of water when covered by an oil film. The oil cuts down the rate of evaporation very much but has practically no effect on the partial pressure of water at equilibrium. Taylor[69] points out that normally the time of contact between a gas and the solid catalytic agent is extremely small and consequently anything which decreases the rate of adsorption will cut down the reaction velocity very much.

It is easy to see that the piling up of the reaction products will cut down the reaction velocity, if they prevent the reacting substances from coming in contact with the catalytic agent. This has been observed in the contact sulfuric acid process.[70] The explanation that the decrease in the reaction velocity is due to a decreased adsorption of the reacting substances was first given by Fink,[71] who is the real pioneer in this line. Although the reaction between carbon monoxide and oxygen is practically irreversible at ordinary temperatures, Henry[72] recognized that the presence of the reaction product might slow up the rate of reaction and he proved his point by increasing the reaction velocity when he removed the carbon dioxide with caustic potash. Water vapor checks the catalytic dehydration of ether[73] and of alcohol[74] and hydrogen cuts down the catalytic dehydrogenation of alcohol.

W. C. McC. Lewis[75] points out that the explanation of the poisoning of catalytic agents on the basis of adsorption leads to certain conclusions in regard to the temperature coefficient.

> One of the chief difficulties met with in the kinetics of heterogeneous reactions has its origin in the selective nature of the adsorbability of the reactions and the resultants, particularly the latter. The so-called catalytic poisons are now generally regarded as owing their effect to marked selective adsorption, as a result of which the surface of the catalyst becomes covered with a layer of molecules and is thus no longer capable of catalyzing the reaction. In many cases the resultants of the reactions are adsorbed in this manner and consequently function as a catalytic poison. Since the extent of adsorption diminishes as the temperature rises, it is obvious that when such poisoning effects are present, the temperature coefficient of the reaction

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[56] Taylor, *Trans. Am. Electrochem. Soc.*, **36** (1919), 149.

[57] Bancroft, *J. Phys. Chem.*, **21** (1917), 734.

[58] *Wied. Ann.*, **35** (1888), 903.

[59] "Experimental Researches on Electricity," **1** (1839), 185.

[60] *Z. anorg. Chem.*, **16** (1896), 50.

[61] *J. Am. Chem. Soc.*, **42** (1921), 1285.

[62] *J. prakt. Chem.*, **29** (1843), 238.

[63] *J. Chem. Soc.*, **115** (1919), 1050.

[64] *Ibid.*, **117** (1920), 1280, 1501; **119** (1921), 225.

[65] *Ber.*, **51** (1918), 1743.

[66] *J. Am. Chem. Soc.*, **38** (1916), 2272.

[67] *Ibid.*, **38** (1916), 1145.

[68] *Ibid.*, **42** (1920), 372.

[69] Taylor, *Trans. Am. Electrochem. Soc.*, **36** (1919), 149.

[70] Bodlander and Koppen, *Z. Elektrochem.*, **9** (1903), 566; Berl, *Z. anorg. Chem.*, **44** (1905), 267.

[71] Bodenstein and Fink, *Z. physik. Chem.*, **60** (1907), 61.

[72] *Phil. Mag.*, [3] **9** (1836), 324.

[73] Ipatieff, *Ber.*, **37** (1904), 2996.

[74] Engelder, *J. Phys. Chem.*, **21** (1917), 676.

[75] *J. Chem. Soc.*, **115** (1919), 182.

velocity over a certain range of temperatures is not comparable with that over a different range, for the total observed velocity depends only on the true effect of temperature on the chemical process itself, but likewise on the alteration in the extent of active surface presented to the reactants. The simplest conditions are obviously those in which the adsorption effects are a minimum, and such conditions will occur generally when the energy required for sublimation or desorption is small. In other cases, where adsorption effects are large, it is necessary to correct the observed velocity constants for the change in the area of the effective surface produced as a result of the change in temperature. Thus in the case in which the resultant is markedly adsorbed, and therefore acts as a negative catalyst, the temperature coefficient will possess too high a value and, instead of decreasing as temperature rises, may even increase. A similar abnormal behavior is to be anticipated when a reaction proceeds partly in the homogeneous gaseous phase, partly in the surface, for, as the temperature rises, the reaction tends to predominate in the gaseous phase, and therefore possesses a higher temperature coefficient.

We have seen that the poisoning of a catalytic agent is due to marked adsorption, which cuts down the adsorption of the reacting substances. We have also seen that the presence of sulfur trioxide tends to decrease the rate of reaction of sulfur dioxide and oxygen. We can now imagine a hypothetical case in which one of the reaction products is adsorbed so strongly that it acts as a poison. In that case we shall get entirely different results depending on the amount of catalytic agent present. If there is a large excess of catalytic agent the reaction will run to an end or to true equilibrium before the catalytic agent is entirely poisoned. If, on the other hand, there is only a small amount of catalytic agent, it will be poisoned very early in the course of the reaction, and we shall have an apparent equilibrium reached from only one side which will vary with the amount of catalytic agent. For any given amount of catalytic agent we shall get an apparently definite end-point; but the value of the end-point will vary with the amount of catalytic agent taken. At least one case of this sort has been recognized definitely. Neilson[76] has studied the splitting of salicin and amygdalin by platinum black.

It is found that the amount of splitting of salicin in a given time reached a maximum, and then with increasing time the amount of splitting was not proportional to the time, being materially less in the last twenty-four hours than it was in the preceding. This is due, no doubt, to the effect of the products of the splitting—especially the saligenin. It is more probably due, however, to the salicylic acid produced by the oxidation of saligenin to salicylic acid by the platinum. It is well known that salicylic acid has a marked retarding action on enzymes as shown by Kastle and Loevenhart[77] in its action on lipase; and by Neilson[78] in its action on platinum black in the hydrolysis of ethyl butyrate.

The experiments with amygdalin and platinum black were carried out in the same way as those with salicin. It was anticipated, however, that the amount of splitting by the action of platinum black on the amygdalin would be small, as it is well known from Bredig's work on the catalysis of hydrogen peroxide by colloidal platinum,[79] and from Neilson's[78] work on the hydrolysis of ethyl butyrate by platinum black, that hydrocyanic acid has a marked retarding action on the catalytic action of platinum. One of the splitting products of amygdalin is hydrocyanic acid; and according to the above experiments one would expect the action of platinum black on amygdalin to be retarded, if not stopped entirely. Such, indeed, was found to be the case, as the first experiment with tightly corked flasks was entirely negative. It occurred to me that by leaving the flasks uncorked the hydrocyanic acid would volatilize and the action would then proceed. This is in keeping with the well-known fact that removing one of the products of a chemical reaction allows the action to go on to completion. By leaving the flasks uncorked it was found by a qualitative test that platinum splits up the amygdalin. It was further seen that the action did not go on to completion, as the amount of sugar produced was small.

Since enzymes are poisoned by many substances in something the same way that colloidal platinum is, it seems worth while to see whether autotoxic catalysis would account for some of the peculiarities in enzyme action which have puzzled people. If autotoxic catalysis occurs, we should expect that the presence of the reaction products would cut down the reaction velocity even though the reverse reactions were negligible. If the poisoning action of the reaction products is sufficient we should get false equilibria if we started with small amounts of the enzymes and the reaction would run to an end if we took larger amounts of the enzymes. Both these phenomena have been observed.[80]

The poisoning of colloidal platinum in its action on hydrogen peroxide solutions is undoubtedly due to adsorption; but we have no direct measurements on the adsorption and consequently we do not know positively that this is the right explanation and we do not know that there may not be other factors which have been overlooked.

PROTECTING COLLOID AS POISON

One possible disturbing factor may be the presence of a protecting colloid added to stabilize a metal hydrosol.[81]

The rate of decomposition of hydrogen peroxide by colloidal platinum has been made use of in determining the absolute and relative influences of different protective colloids upon the colloidal metal,[82] the times required for the decomposition of a definite percentage of the peroxide under varying conditions being noted. With gelatin the results are typical, and are given in the following table:

Percentage of Gelatin	Relative Times Required to Decompose 50 Per cent of the Peroxide Solution
0.00	100
0.001	437
0.01	460
0.05	620
0.10	983

It will be noticed that even small quantities of gelatin exert a most important influence, retarding the decomposition of the peroxide very considerably, as is usual with a protective colloid. The gelatin, however, increases the stability of the colloidal metal solution, and tends to prolong its period of activity by preventing its precipitation by electrolytes, thereby enabling many reactions to be studied other than the decomposition of pure hydrogen peroxide solution.

Similar results have been obtained by Rideal[83] and by Iredale.[84] While these are just what might have been predicted, there is no explanation at the moment for the results of Paal and Hartmann[85] that addition of colloidal cupric hydroxide increases the action of a palladium hydrosol on oxyhydrogen gas, while addition of colloidal zinc hydroxide first retards and then increases the rate of reaction. Mercury displaces hydrogen from a palladium hydrosol[86] and decreases the catalytic action on oxyhydrogen gas. It does not destroy the catalytic action on hydrogen peroxide, presumably because mercury itself decomposes hydrogen peroxide catalytically.

EARLY VIEWS ON POISONING

It is interesting to note that as far back as 1857 Bunsen perceived clearly that the removal of the reaction products is essential to the continued action of the catalytic agent. Speaking of the catalytic action of platinum and manganese dioxide on hydrogen peroxide, Bunsen[87] says that "it is only when the products of decomposition are removed by foreign forces, such as gravitation, capillarity, expansion, etc., and by means of these foreign forces new matter is brought into contact, that the phenomenon is repeated."

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[76] *Am. J. Physiol.*, **15** (1906), 148.

[77] *Am. Chem. J.*, **24** (1900), 491.

[78] *Am. J. Physiol.*, **10** (1903), 197.

[79] Bredig, "Anorganische Fermente," **68** (1900).

[80] Tammann, *Z. physik. Chem.*, **18** (1895), 426; Kastle and Loevenhart, *Am. Chem. J.*, **24** (1900), 491.

[81] Friend, "A Textbook of Inorganic Chemistry," **9-I** (1920), 271.

[82] Gröh, *Z. physik. Chem.*, **88** (1914), 414.

[83] *J. Am. Chem. Soc.*, **42** (1920), 740.

[84] *J. Chem. Soc.*, **119** (1921), 109.

[85] *Ber.*, **51** (1918), 894.

[86] Paal and Steger, *Ibid.*, **51** (1918), 1743.

[87] *J. Chem. Soc.*, **26** (1873), 736.

Debus[88] has considered the question of effective collisions and has anticipated some of Langmuir's views on oriented adsorption.

> Whenever two mols of peroxide of hydrogen meet in the *position of reaction*, then decomposition into water and oxygen will take place, but if they collide in other positions, then they will not decompose. * * * * The decomposition of peroxide of hydrogen into water and oxygen is retarded by some and accelerated by other substances. Platinum, silver oxide, and manganic dioxide, respectively, promote, whilst acids prevent the decomposition. Platinum possesses a great attraction for oxygen, its powder absorbs more than two hundred times its volume of the gas. This attraction is also exerted towards oxygen which is in chemical combination.
>
> If now a piece of platinum is placed in peroxide of hydrogen, the molecules of the latter will place themselves in such a position of the surface of the platinum, that one oxygen atom of the peroxide is turned towards the platinum and as near to it as possible. The peroxide is polarized. But this has the effect also of bringing the oxygen atoms of different molecules of peroxide in such close proximity on the surface of the metal that they can combine to form common oxygen, the decomposition of the peroxide into water and oxygen and development of energy being the consequence. The action of the platinum places the molecules of the peroxide in *the position of reaction* towards each other. The actions of silver oxide and of black oxide of manganese are similar.

There are a couple of interesting cases of what appears to be poisoning of the catalytic agent; but the data are not sufficient to warrant very definite conclusions.[89] Phosgene reacts with water to give carbon dioxide and hydrochloric acid,

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

So far as is known, this reaction is not reversible and it actually runs to an end in presence of an excess of water. In presence of concentrated hydrochloric acid, however, the rate of hydrolysis is practically negligible. The most plausible way of accounting for this is by assuming that water and phosgene do not react by themselves and that the reaction takes place solely in contact with the walls of the containing vessel. When these are coated with a film of hydrochloric acid of sufficient concentration, practically no phosgene is adsorbed and no reaction takes place. The hydrolysis should be studied with different concentrations of hydrochloric acid and with a varying ratio of wall surface to mass of solution. If this explanation is correct, it may account for the rather surprising stability of a phosgene cloud in the damp atmosphere of Flanders, there being no catalytic agent in the cloud to cause the decomposition of the phosgene. On this basis, a cloud consisting of a mixture of hydrochloric acid and phosgene would be even more stable; but of course this would introduce serious complications in regard to loading.

Trimethylchloroformate, $ClCO_2CCl_3$, or superpalite as it is called, decomposes to carbon tetrachloride and carbon dioxide in presence of alumina,

$$ClCO_2CCl_3 = CO_2 + CCl_4,$$

and to phosgene in presence of ferric oxide,

$$ClCO_2CCl_3 = 2COCl_2.$$

The reverse reaction has never been made to take place to any measurable extent. During the war some superpalite and ferric oxide were placed in a glass tube connected with a closed manometer. There was rapid decomposition at first, as shown by the increase in pressure; but, before long, the reaction apparently came to an end. On raising the temperature, the reaction went a little farther and did not reverse when the temperature was brought back to its original value. Since this experiment was not repeated there may be some error in it and the facts may not be as stated; but it looks as though the ferric oxide was poisoned and as though the change of temperature modified the adsorption so that more superpalite came in contact with the catalytic agent and was decomposed. If this is the true explanation, it suggests one interesting set of experiments. When ethyl butyrate and water are treated with a small amount of lipase,[90] the decomposition proceeds only a little way, owing to the poisoning of the enzyme by the reaction products.[91] It seems probable that with an oscillating temperature it might be possible to carry the reaction much farther with the same amount of enzyme.

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[88] *J. Chem. Soc.*, **53** (1888), 327; Cf. Hüfner, *J. prakt. Chem.*, [2] **10** (1874), 385; Raschig, *Z. angew. Chem.*, **1906**, 1078; Gillet, *Bull. soc. chim. Belg.*, **30** (1921), 138.

[89] Bancroft, *Trans. Am. Electrochem. Soc.*, **36** (1919), 140.

[90] Kastle and Loevenhart, *Am. Chem. J.*, **24** (1900), 491.

[91] Bancroft, *J. Phys. Chem.*, **22** (1918), 40.

(*To be continued*)

Isotopes

By G. M. J. Mackay

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The attention of chemists is called to the remarkable developments which are being made in our knowledge of the fundamental structure of matter and energy. The work of the Cavendish Laboratory in the last few years leaves but little doubt that our complicated system of elements is in reality built up from two simple units, the electron and the proton, the latter being the real unit of mass, the atom of positive electricity, and identical with the nucleus of the hydrogen atom. The work of Rutherford and his associates has shown that artificial radioactivity may be stimulated in the ordinary elements. Hydrogen has been expelled by alpha particles, which are but positively charged helium atoms traveling at a velocity imparted by 6,000,000 volts, from the atoms of nitrogen, boron, fluorine, sodium, aluminium, and phosphorus. In many cases this expulsion is accompanied by an evolution of energy, in the case of aluminium of 40 per cent more than that possessed by the helium projectile.

Lately, Dr. F. W. Aston, who has been delivering a course of lectures at the Franklin Institute, has found that most of the elements of fractional atomic weights are really composed of isotopes whose atomic weights are integers to an accuracy of one part in a thousand. At the same time he has found another possible source of interatomic energy. His work is a masterpiece of ingenuity and skilled technic, and is an illustration of the value of tireless perseverance in searching for the meaning of apparently trivial deviations of numerical results from one another. A synopsis of a lecture by Dr. Aston before the local branches of the American Institute of Electrical Engineers and the American Chemical Society at Schenectady on April 7, 1922, follows:

> In 1803 John Dalton gave to chemistry what is probably one of the greatest generalizations in its history, the atomic theory. All of his five postulates have since stood the test of over a century of active and unremitting investigation except the one which states that "atoms of the same element are similar to one another and equal in weight."
>
> No direct method was available for testing this hypothesis until 1910, when Sir J. J. Thomson showed that sharply defined parabolic streaks were obtained on a photographic plate when beams of positively charged ions were deflected by means of magnetic and electrostatic fields. This proved that the ratio of the charge of electricity to the mass of the particle was constant for all the ions forming the parabola, and since the charge was known to be a definite unit, that the masses of the individual atoms were approximately the same. But the apparatus was not sufficiently accurate to detect small variations in weight.

However, indirect evidence that there might be different atoms of the same element was forthcoming from the work of Sir Ernest Rutherford and others. Investigations of the transformations undergone by different radioactive families showed that lead could be formed in several ways. Each kind of lead was found to be identical chemically with the others, but the atomic weights calculated from that of the original substance by subtraction of the masses of the alpha particles emitted in the radioactive transformations indicated that the atomic weights must be different. Thus lead from the uranium series should have an atomic weight of 206, lead from thorium 208, while ordinary lead has a weight of 207.2. Careful investigation of lead from various radioactive minerals by Richards, Soddy, Hönigschmidt, and others showed differences in their atomic weights which by far exceeded the possible experimental error.

F. W. Aston

These substances which have different atomic weights but the same position in the periodic table were called "isotopes" by Professor Soddy.

Moseley's epoch-making discovery has shown us that the chemical properties of the elements have nothing whatever to do with their atomic weights but do depend on a much more fundamental factor, the atomic number, or the number of positive charges on the nucleus of the atom. Isotopes may be shortly defined, therefore, as elements having the same atomic number but different atomic weights.

The first indication that the nonradioactive elements might also have isotopes was given by Sir J. J. Thomson, when he announced that when neon was analyzed by the positive ray method, two parabolas were indicated, corresponding to the atomic weights 20 and 22. In 1913 Aston succeeded in fractionating these two gases by diffusion through pipe clay and obtained two parts differing by 0.7 per cent in density. This result is in agreement with the separation theoretically possible, as determined from later and more accurate work.

After the war Dr. Aston continued this investigation with the idea of making the method of analysis so accurate that the atomic weights of the gases in question would be definitely settled.

In order to do this he radically modified Thomson's positive ray apparatus, so that atomic masses can now be determined to an accuracy of one part in a thousand.

By the application of specially designed magnetic and electrostatic fields to positively charged ions emerging from a narrow slit in the cathode of an electrical discharge tube, he is able to deflect beams of ions which come to a focus on a photographic plate. Each line is produced only by charged atoms having exactly the same atomic weight, and the lines due to different atoms are separated by distances proportional to their masses. Thus a mixture of atoms can be separated into rays of particles having equal mass in an analogous way to the resolution of ordinary light by the spectrograph into its components of different wave lengths. On account of this similarity the instrument has been called a positive ray spectrograph, and the spectrum produced, a mass spectrum.

When neon was subjected to analysis in this way it was found that lines corresponding to atomic weights of exactly 20 and 22 made their appearance. The latter line was much fainter than the former, as it should be, since only 10 per cent of the heavier isotope is required to make the mean atomic weight of ordinary neon 20.2.

Similar analyses were then made of as many of the elements as possible, with the result that many of our supposedly simple elements have been resolved into two or more isotopes. The following table summarizes the results thus far obtained:

ELEMENT	Atomic Number	Atomic Weight	Minimum Number of Isotopes	Masses of Isotopes in Order of Their Intensity
H	1	1.008	1	1.008
He	2	3.99	1	4.0
Li	3	6.94	2	7, 6
B	5	10.9	2	11, 10
C	6	12.0	1	12
N	7	14.01	1	14
O	8	16	1	16
F	9	19	1	19
Ne	10	20.2	2	20, 22, 21?
Na	11	23	1	23
Mg	12	24.32	3	24, 25, 26
Si	14	28.3	2	28, 29, 30?
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37, 39?
A	18	39.88	2	40, 36
K	19	39.1	2	39, 41
Ca	20	40.09	1	40 (39, 40, 41)
Ni	28	58.68	2	58, 60
Zn	30	65.4	3	64, 66, 68, (70)
As	33	74.96	1	75
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
Rb	37	85.45	2	85, 87
I	53	126.92	1	127
Xe	54	130.20	5 (7?)	129, 132, 131, 134 136, 128? 130?
Cs	55	132.81	1	133
Hg	80	200.6	6	197–200, 202, 204

The most significant result of these measurements is that, with the exception of hydrogen, the weights of all the elements measured are whole numbers to an accuracy of 0.1 per cent. Also the relative positions of potassium and argon, nickel and cobalt, are reconciled with the order of increasing mass in the periodic table.

This immediately revives the original hypothesis of Prout, suggested in 1815, that atoms were themselves built up from particles of Protyle, which he endeavored to identify with hydrogen. The modern development of this idea is that the ultimate particles of matter are composed of atoms of positive electricity, or protons, and the atoms of negative electricity, or electrons. The proton appears to be the real unit of mass and is identical with the nucleus of the hydrogen atom.

Since isotopes are identical in their chemical behavior, physical methods only are available for their separation. Neon has been partly separated into its constituents by Aston; chlorine, by Harkins, and mercury, by Brönsted and Hevesy.

Since hydrogen has an atomic weight greater than unity, one would naturally expect that when four atoms of hydrogen combine to form an atom of helium the resulting atomic weight would be 4.032 instead of exactly 4.00. When the positive and negative charges of the hydrogen, which are relatively very far apart, are compressed into the helium nucleus, from the electromagnetic theory of mass, a loss of mass due to "packing" should occur. But when mass is annihilated, energy should appear, and assuming the loss of mass as measured, it may be calculated that if the hydrogen in 9 cc. of water were transformed to helium 200,000 kw. hrs. would be evolved. Dr. Eddington believes that this answers the riddle of why the sun keeps hot, since if 10 per cent of the hydrogen present in the sun condenses to form helium, enough energy would be supplied to maintain the present temperature for 1,000,000,000 years.

Chemical Plant Equipment Manufacturers

The organization committee of the Association of Chemical Plant Equipment Manufacturers will call a meeting in New York for the purpose of completing the organization of this Association. The following program has been arranged:

On Tuesday, May 9, at 8 o'clock, the members of the Association will be addressed by Dr. Julius Klein, of the U. S. Department of Commerce, and Mr. E. W. McCullagh, Manager of the Fabricated Production Department of the U. S. Chamber of Commerce.

On Wednesday morning, May 10, at 10 o'clock, the organization meeting will be held and the formal organization will be completed. At 2:00 P.M., the members of the Association will be addressed by Mr. Charles Roth, of the Chemical Exposition Show, Mr. Campbell, of the Boston Textile Show, Mr. Reeves of the New York Automobile Show, and Mr. Ebertt, of the Ice Cream Supply Dealers Association.

These meetings will be held at the Chemists' Club, 52 E. 41st St., New York City.

The Atlas Valve Company of Newark, N. J., has announced the production of an automatic low water shut-off valve made especially for application to gas fired steam boilers.

SCIENTIFIC SOCIETIES

Calendar of Meetings

American Oil Chemists' Society—13th Annual Meeting, New Orleans, La., May 8 and 9, 1922.

American Zinc Institute—St. Louis, Mo., May 8 and 9, 1922.

Institute of Metals Division of A. I. M. E.—Rochester, N. Y., June 5 to 9, 1922.

National Fertilizer Association—29th Annual Convention, White Sulphur Springs, W. Va., week of June 12, 1922.

American Institute of Chemical Engineers—14th Semiannual Meeting, Niagara Falls, Ontario, June 19 to 22, 1922.

American Leather Chemists Association—19th Annual Meeting, Ontario, Canada, June 21 to 23, 1922.

Alpha Chi Sigma Fraternity—7th Biennial Conclave, St. Louis, Mo., June 22 to 24, 1922.

American Society of Testing Materials—25th Annual Meeting, Atlantic City, N. J., June 26 to July 1, 1922.

Sixty-third Meeting, American Chemical Society, Birmingham, Alabama, April 3 to 7, 1922

Program of Papers

GENERAL MEETING

Hon. Nathan L. Miller, Lieutenant Governor of Alabama. Address of Welcome.

Edgar F. Smith, President, American Chemical Society. Response.

Carlile P. Winslow, Director, U. S. Forest Products Laboratory. The Development of the Forest Products Industry in the South.

William H. Stone, Associate Editor, *Manufacturers Record*. The Remarkable Development of the South and Its Relations to the American Chemical Industry.

Theodore Swann. The Manufacture of Phosphoric Acid in the Electric Furnace by the Condensation and Electrical Precipitation Method.

Van H. Manning. The Pioneer's Field in Petroleum Research.

Charles L. Reese. Informational Needs in Science and Technology.

W. C. Geer. Recent Developments of the Chemistry of Rubber.

W. D. Bigelow. Some Research Problems in the Canning Industry.

Francis P. Venable. Chemistry in the Old South and the New.

PUBLIC MEETING

Marston Taylor Bogert, Past President, American Chemical Society. The Flower and the Organic Chemist. Perfumes—Natural and Synthetic.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

T. J. Bryan, *Chairman* C. S. Brinton, *Secretary*

1. Benjamin R. Jacobs. Composition, Grade and Baking Qualities of Self-Rising Flours.
2. Juanita E. Darrah. Bleached and Self-Rising Flours.
3. Juanita E. Darrah. Composition and Nutritive Value of Yeast Grown in Vitamin-Free Media.
4. Juanita E. Darrah. New Sources of Water-Soluble C and Fat-Soluble A in the Southeast.
5. Edward Gudeman. Foods, Facts, Fancies, and Follies.
6. Edward F. Kohman. The Determination of Hydrogen Sulfide Evolved by Foods when Cooked at Various Temperatures.
7. C. S. Robinson. Studies of the Availability of Organic Nitrogenous Compounds—II. (By title.)
8. R. O. E. Davis. The Interpretation of Mechanical Analysis of Soils as Affected by Soil Colloids.
9. J. W. Sale and J. B. Wilson. Determination of Methyl Anthranilate.
10. J. B. Wilson and J. W. Sale. Determination of Methanol.
11. Edgar T. Wherry. Relations between the Active Acidity and the Lime Requirements of Soils.
12. M. F. Showalter and R. H. Carr. Characteristic Proteins in High and Low Protein Corn.
13. E. G. Mahin and R. H. Carr. Errors in the Determination of Fat in Cream.
14. William H. Ross, C. B. Durgin and R. M. Jones. The Commercial Purification of Phosphoric Acid by Crystallization.
15. E. R. Miller. Do Velvet Beans Contain Vitamin B?
16. B. B. Ross. The Occurrence and Composition of Some Alabama Phosphates.
17. H. H. King and M. C. Sewell. The Mineral Requirements for the Nutrition of Wheat during the Seedling Phase. (Lantern.)
18. E. H. S. Bailey. A Dietary Study of Some State Institutions.
19. Floyd W. Robison. Studies on the Electropure Process of Treating Milk. (Lantern.)
20. J. S. McHargue. The Role of Manganese in Plants. (Lantern.)
21. W. O. Robertson. The Absorption of Water by Soil Colloids.

BIOLOGICAL CHEMISTRY

Howard B. Lewis, *Chairman* J. S. Hughes, *Secretary*

1. J. C. Swenarton and E. Emmet Reid. Higher Alcohols Formed in the Fermentation of Sugar.
2. James F. Couch. The Toxic Constituent of Greasewood (*Sarcobatus vermiculatus*).
3. C. L. Hare. Influence of Breeding upon Oil and Protein Content of Cottonseed.
4. Jack Montgomery. The Iodine Absorption of Urine.
5. E. R. Miller. Influence of Sodium Chloride upon Animal Excretion.
6. Atherton Seidell. Further Experiments on the Isolation of Vitamin.
7. C. H. Hunt and A. R. Winter. Cow's Milk *vs.* Goat's Milk as a Source of Vitamin C. (Lantern.)
8. J. S. Hughes and H. B. Winchester. Results Obtained by Feeding Breeding Gilts a Ration Low in Fat-Soluble Vitamin. (Lantern.)
9. J. S. Hughes, L. D. Bushnell and L. F. Payne. The Influence of Vitamin Content of a Feed on the Immunity to Roop. (Lantern.)
10. Harper F. Zoller. The Detection and Estimation of Inorganic Activators in Commercial Rennin and Pepsin Preparations.
11. Harper F. Zoller. A Laboratory Disinfectant to Displace Mercuric Chloride Solutions.
12. I. K. Phelps and J. E. Basch. The Decomposition of Food by *Bacillus botulinus*.
13. Max Kahn. The Feeding of Non-Ketogenic Odd-Carbon Fats to Diabetic Patients. (By title.)
14. Arno Viehoever and Ruth G. Capen. A New Source of Santonin.
15. Victor E. Levine. A New Method for the Colorimetric Determination of Peroxidase.
16. Victor E. Levine. A Simple Method for Differentiating Boiled or Pasteurized Milk from Unboiled or Unpasteurized Milk.
17. Victor E. Levine. Selenium Compounds as Biochemical Reagents.
18. Victor E. Levine and Arthur C. Antony. The Catalytic Properties of the Metals Occurring in Respiratory Pigments.

CELLULOSE CHEMISTRY SECTION

Harold Hibbert, *Chairman* G. J. Esselen, Jr., *Secretary*

1. Report of the Standard Cellulose Committee.
2. Report of the Analytical Methods Committee.
3. Report of the Viscosity Measurement Committee.
4. E. C. Sherrard and A. W. Froehlke. The Effect of Concentrated Hydrochloric Acid on Different Celluloses.
5. E. C. Sherrard and W. H. Gauger. The Effect of Salts upon the Acid Hydrolysis of Wood.
6. E. C. Sherrard and C. F. Suhn. Sugar Formation in a Sulfite Digester.
7. E. C. Sherrard. Ethyl Alcohol from Western Larch.
8. E. C. Sherrard and G. W. Blanco. Some of the Products Obtained in the Hydrolysis of White Spruce Wood with Dilute Sulfuric Acid under Steam Pressure.
9. L. F. Hawley and S. S. Aiyar. The Distribution of Methoxyl in the Products of Wood Distillation.
10. G. J. Ritter and L. C. Fleck. The Chemistry of Wood—V.
11. S. A. Mahood and D. E. Cable. The Chemistry of Wood. IV—The Analysis of Western White Pine and Eucalyptus.
12. S. A. Mahood. Some Observations on the Determination of Cellulose in Woods—II.
13. W. O. Mitscherling. Preparation of a "Standard Cellulose."
14. Harold Hibbert and Harold S. Hill. Synthesis of Derivatives Relating to Polysaccharides.
15. Harold Hibbert and John A. Timm. Synthesis and Properties of Cyclic Acetal Derivatives.
16. Harold Hibbert. Constitution of Sedoheptose Anhydride and Its Relation to Cellulose.

17. Symposium. The Action of Alkali and Acid on Cellulose, Wood and Waste Cellulosic Material with Special Reference to the Production of Cheap Cattle Foods.
18. Joint Symposium with Division of Organic Chemistry. Recent Work on the Constitution of Starch and Cellulose.

CHEMICAL EDUCATION SECTION

Edgar F. Smith, *Chairman* Neil E. Gordon, *Secretary*

An Ideal First Year Course in Chemistry

1. William McPherson. First Year College Chemistry.
2. Wilhelm Segerblom. High School Chemistry.
3. Miss Minnie B. Fisher. First Year Chemistry for Women.
4. Eugene C. Bingham. Teaching of the Metric System in First Year Chemistry.
5. F. P. Venable. Methods for Presenting First Year Chemistry.
6. Neil E. Gordon. Teaching First Year Chemistry by the Project Method.

Chemical Engineering Education

7. W. K. Lewis and R. T. Haslam. Studying Chemical Engineering by the Unit-Operation Method.
8. J. L. Daniel. Standardization of Courses in Quantitative Analysis for Students in Chemical Engineering.
9. R. H. McKee. Discussion of Committee's Report on Chemical Engineering Education.
10. L. J. Desha. Correlation of Engineering Thermodynamics with Chemical Thermodynamics.
11. C. S. Williamson, Jr. Importance and Time Given for Courses in Economics and Industrial Management in Chemical Engineering Training.
12. Graham Edgar. Distribution of Time between "Pure" and "Applied" Science.

Round-table discussion.

13. Marston Taylor Bogert. Recent Progress at Columbia University.
14. J. N. Swan. Some Laboratory Helpers.
15. Charles W. Cuno. A Chart of the Synthetic Intermediates.
16. H. A. Webb. Standard Test in Science, especially Chemistry.
17. W. F. Hand. Training for Agricultural Chemistry.
18. Jack P. Montgomery. Unified Chemistry Courses.
19. Edward G. Mahin. Science or Athletics?

DYE CHEMISTRY DIVISION

William J. Hale, *Chairman* R. Norris Shreve, *Secretary*

1. Herbert L. Haller. The Preparation of Phenylglycine-*o*-carboxylic Acid. I—From Anthranilic Acid and Monochloroacetic Acid. (Lantern.)
2. Max Phillips. On the Preparation of 7,7'-Di(-hydroxy-isopropyl)-indigo.
3. S. Palkin. A New Method for the Preparation of Dicyanine and Related Dyes. (By title.)
4. C. R. DeLong and W. N. Watson. The Necessity for Reclassification and Standardization of Dyes.
5. W. R. Waldron and E. Emmet Reid. The Influence of Sulfur on Colors of Azo Dyes.
6. Marston Taylor Bogert and Martin Meyer. Experiments with Dehydrothio-*p*-toluidine and Related Compounds.
7. Jules Bebie. Uses of *p*-Toluene-sulfonyl Chloride in the Manufacture of Dyes and Intermediates.
8. Andrew J. Leddy. The Method of Determining the Class to Which Each Dye Belongs.
9. Andrew J. Leddy. The Function of Assistants Used in Dyeing Cotton.
10. Walter C. Holmes. The Application of the Direct Dyes in Coloring Paper.
11. R. E. Rose. The Functions of the Dye Testing Laboratory.
12. Henry R. Lee and D. O. Jones. The Analysis of β-Naphthylamine.

HISTORY OF CHEMISTRY SECTION

C. A. Browne, *Chairman* Lyman C. Newell, *Secretary*

1. Edgar F. Smith. Dr. Thomas Cooper—A Pioneer American Chemist.
2. C. A. Browne. Several Early References Pertaining to Chemical Warfare.
3. George L. Coyle. The Chemical and Scientific Achievements of Father Athanasius Kircher, S. J.
4. Ralph H. McKee. Some Photographic Reminiscences of the Priestley Centennial of 1874.
5. John N. Swan. A Book and a Battery.
6. J. A. Gunton. An Early Type of Chemical Slide-Rule.
7. William McPherson. Reminiscences of Italian Chemists.

Symposium on the History of Early Chemical Industries in America, More Particularly of Those in the South

8. C. A. Browne. A Few Sources of Information upon Early Chemistry and Chemical Industries in America.
9. B. B. Ross. Some Facts Relating to Early Chemists and Chemical Industries in Alabama.
10. Elton R. Darling. History of the Early Salt Industry of the Ohio River and Kanawha Valley.
11. Eugene A. Smith. Some Early Southern Chemists and Their Work.

INDUSTRIAL AND ENGINEERING CHEMISTRY

W. K. Lewis, *Chairman* E. M. Billings, *Acting Secretary*

I—Symposium on Distillation

W. A. Peters, Jr., *Chairman*

1. W. A. Peters, Jr. Efficiency and Capacity of Fractionating Columns. (Lantern.)
2. Clark S. Robinson. The Plate Efficiency of a Continuous Alcohol Still.
3. W. K. Lewis and Clark S. Robinson. The Simple Distillation of Hydrocarbon Mixtures.
4. S. S. Heide. Benzene Purification.
5. C. A. Lambert. Wood Turpentine.
6. W. K. Lewis and Harold C. Weber. The Calculation of the Heats of Vaporization of Various Liquids, First, by Means of the Hildebrand Function; Second, from Vapor Pressure Curves.
7. J. W. Bodman. Present Practice of Dynamite and Chemically Pure Glycerol Distillation.
8. McGarvey Cline. Turpentine Distillation.

II—General Papers

9. A. C. Fieldner and G. W. Jones. Carburetor Adjustment by Gas Analysis. (Lantern.)
10. G. J. Fink. Investigations of Whitewashes and Aqueous Lime Paints. (Lantern.)
11. R. Norris Shreve. Can We Afford to Make Potash in America?
12. L. F. Hawley. Discontinuous Extraction Processes.
13. S. W. Parr. The Classification of Coal.
14. A. C. Fieldner, W. A. Selvig and W. L. Parker. A Comparison of the Standard Gas Furnace and Micropyrometer Methods for Determining the Fusibility of Coal Ash. (Lantern.)
15. S. W. Parr and C. N. Davidson. The Calorific Value of American Woods.
16. S. P. Kinney and G. St. J. Perrott. The Shatter and Friability Tests for Metallurgical Coke.
17. Harold J. Rose. Determination of True Specific Gravity of Coke.
18. G. St. J. Perrott and H. W. Clark. Smokeless Fuel for Salt Lake City.
19. S. W. Parr. The Ultimate Analysis of Coal by Utilization of Sodium Peroxide Fusions.
20. W. D. Collins. The Value of Brands to Buyers.
21. Arthur L. Davis. Acetone, Butanol, Ethanol and Gas from the Butyric Fermentation of Corn.
22. A. F. Thal. Crystallization in Transparent Soap. (By title.)
23. Lloyd Logan. The Control of Industrial Processes by Light Sensitive Means. (By title.)

ORGANIC CHEMISTRY DIVISION

H. T. Clarke, *Chairman* Frank C. Whitmore, *Secretary*

1. M. C. Sneed and J. Louis Maynard. Preparation of Methylmercuric Acetate and Methylmercuric Hydroxide.
2. Henry C. Howard, Jr., and J. Louis Maynard. An Electrolytic Method for the Preparation of Mercury Dimethyl from Methylmercuric Hydroxide.
3. William A. Noyes and H. M. Chiles. The Asymmetry of Diazodiethyl Glutarate.
4. L. Charles Raiford and Liang Yi Ho. Further Observations on the Nitration of Halogenated Phenols.
5. Marston Taylor Bogert and Y. G. Chen. New Organic Selenium Compounds.
6. Marston Taylor Bogert and E. Abrahamson. The Synthesis of a Thiazole Analog of Cinchophen (Atophan).
7. Edward C. Franklin. Hydrocyanic Acid: An Ammono Carbonous Acid and an Ammono Formaldehyde.
8. Henry Gilman and Charles H. Meyers. A Study of the Optimum Condition for the Formation of the Grignard Reagent.
9. Henry Gilman and Harry L. Morris. The Reaction between Thionyl Aniline and the Grignard Reagent.
10. W. Lee Lewis and R. S. Bly. Arsenated Heterocyclic Compounds Prepared from 3,4-Diamino-phenylarsonic Acid.
11. W. Lee Lewis and H. W. Stiegler. Derivatives of the β-Chlorovinyl Arsines.
12. Francis D. Dodge. Chemical and Crystallographic Notes on the Acid Phthalates.
13. Francis D. Dodge. The Occurrence of Formic Acid in Essential Oils.
14. De Witt Neighbors, S. M. Clark, J. E. Miller, A. L. Foster and J. R. Bailey. Catalytic Reduction of the C-N Complex.
15. Harold Hibbert and Harold S. Hill. The Preparation of Mono- and Parabromoacetaldehyde and Their Application to Synthetic Work in Cellulose Chemistry.

16. Harold Hibbert and Roland R. Reed. The Electrolytic Reduction of Crotonaldehyde.
17. C. S. Adams and C. E. Boord. Absorption Spectra of Phenylazophenol and Its Derivatives in the Visible Region. (Lantern.)
18. L. B. Sebrell and C. E. Boord. Preparation and Properties of 1-Mercaptobenzothiazole and Its Derivatives. (Lantern.)
19. C. S. Palmer and Roger Adams. The Condensation of Primary Aromatic Arsines with Aldehydes.
20. Edmund Burrus Middleton and Frank C. Whitmore. Organo-mercury Compounds Formed from Salicylaldehyde and Its Nitro Derivatives.
21. Frank C. Whitmore and Louis Ehrenfeld. Organo-mercury Compounds Formed from Benzenesulfonic and Benzylsulfonic Acids. A Preliminary Report.
22. Jack P. Montgomery. Mass Action in the Preparation of Compounds of Urea with Acids and Salts.
23. T. B. Aldrich and Julia E. Blanner. Mononitro Derivatives of the Benzoic Acid Esters of the Trihalogen Tertiary Butyl Alcohols.
24. E. C. Kendall and A. E. Osterberg. Some Reaction Products of Malonic Ester and Cyclohexane Derivatives.
25. A. B. Brown and E. Emmet Reid. The Alkylation of Aniline.
26. A. B. Brown and E. Emmet Reid. The Amination of Alcohols.
27. T. M. Berry and E. Emmet Reid. The Alkylation of Benzene.
28. Henry Gilman and Chester E. Adams. Ditolyl-ketene.
29. F. B. Flick, H. M. Crawford, R. Hoyle and H. Gilman. The Effect of an *iso* Grouping on the Melting and Boiling Points of Organic Compounds.
30. Henry Gilman and Russell M. Pickens. Physiological Action and Chemical Constitution: The Replacement of the Benzoyl by Related Acyl Groups.
31. W. Lee Lewis and H. C. Cheetham. Arsenated Benzophenone and Its Derivatives—II.
32. W. Lee Lewis and C. S. Hamilton. Arsenated Benzanilide and Its Derivatives.
33. W. L. Evans, C. A. Buehler and R. A. Crawford. The Oxidation of *d*-Glucose, *d*-Mannose and *d*-Galactose with Alkaline Permanganate.
34. Arthur J. Hill and Dewitt T. Keach. Application of Chloro Ethers for the Preparation of Some New Derivatives of Diethyl Malonate and Barbituric Acid.

PETROLEUM CHEMISTRY SECTION

T. G. Delbridge, *Chairman* W. A. Gruse, *Secretary*

1. A. P. Bjerregaard. Volume Changes in Petroleum Products.
2. C. K. Francis and H. T. Bennett. The Surface Tension of Petroleum.
3. W. H. Herschel. The Change in Viscosity of Oils with Temperature. (Lantern.)
4. W. H. Fulweiler and C. W. Jordan. Some Notes on the Determination of the Absolute Viscosity of Petroleum Oils.
5. Thomas Midgley, Jr., and T. A. Boyd. The Compression Values of Blended Motor Fuels.
6. C. J. Rodman. The Catalytic Oxidation of Insulating Oils.
7. R. R. Matthews and P. A. Crosby. Corrosion of Petroleum Refining Equipment.
8. F. E. Hosmer and F. M. Seibert. Recent Developments in the Methods for Extraction of Gasoline from Natural Gas.
9. Edwin DeBarr and F. W. Padgett. Petroleum Education.
10. Conference on the Promotion of Research on Petroleum.
11. C. E. Waters. Sulfur Compounds and the Oxidation of Petroleum Oils. (By title.)

PHYSICAL AND INORGANIC CHEMISTRY

S. E. Sheppard, *Chairman* R. E. Wilson, *Secretary*

1. Robert B. Sosman. Theory of the Structure and Polymorphism of Silica. (Lantern.)
2. Hamilton P. Cady and Howard M. Elsey. A General Conception of Acids, Bases and Salts.
3. Edgar T. Wherry. Crystallography and Atomic Structure. (Lantern.)
4. A. S. Richardson, F. C. Vibrans and W. P. Bell. Equilibrium in the Reduction of Iron Oxides and in the Oxidation of Iron by Steam. (Lantern.)
5. Stewart J. Lloyd. Solubility Measurements on Sulfur Dioxide.
6. Graham Edgar and William H. Schuyler. Esterification Equilibria in the Gaseous Phase.
7. N. E. Gordon and E. Emmet Reid. Partition Ratios and Solubility Numbers.
8. William A. Noyes and Thomas A. Wilson. The Amphoteric Ionization of Hypochlorous Acid.
9. W. V. Evans and Louise Otis. The Ionization of Butyl Mercury Hydroxide.
10. Edward C. Franklin. Ammono Nitric Acid.
11. Eugene C. Bingham and H. L. Young. The Drainage Error in Viscosity Measurements of Viscous Materials by the Capillary Tube Method.
12. Robert H. Bogue. Hydrogen-Ion Concentration and the Properties of the Emulsoid Colloids.
13. S. E. Sheppard and S. S. Sweet. The Elasticity of Ash-Free Gelatin Jellies. (Lantern.)
14. Harry B. Weiser. The Formation of Inorganic Jellies: General Theory.
15. H. H. King and R. W. Wampler. The Adsorption and Orientation of Molecules of Dibasic Organic Acids and Their Ethereal Salts in Liquid-Vapor Interfaces. (Lantern.)
16. B. S. Hopkins and F. H. Driggs. Atomic Weight of Lanthanum.
17. E. B. Starkey and Neil E. Gordon. Thermoregulator. (Lantern.)
18. Jack P. Montgomery. The Concentrations of Alkali Halide Solutions, of the Order of 0.001 *N*, Most Favorable to Adsorption by Barium Sulfate.
19. L. J. Curtman and D. Hart. The Transposition of Insoluble Oxalates by Sodium Carbonate Solution.
20. Louis J. Curtman and N. H. Hecht. A New Method for the Volumetric Determination of Iron.
21. Louis J. Curtman. Two New Pieces of Apparatus for Use in Analytical Work.
22. Graham Edgar and R. B. Purdum. Rapid Electrolysis without Mechanical Stirring.
23. Eugene C. Bingham and Herbert D. Bruce. The Relation of Yield Value and Mobility to the So-called Painting Consistency of Paints.
24. Harry B. Weiser. Hydrous Oxide. IV—Hydrous Stannic Oxide.
25. S. E. Sheppard and S. S. Sweet. The Interfacial Tension between Toluene and Ash-Free Gelatin Solution. (Lantern.)
26. James M. Bell. The Nitration of Toluene.

RUBBER CHEMISTRY DIVISION

C. W. Bedford, *Chairman* Arnold H. Smith, *Secretary*

1. R. P. Dinsmore. Internal Mixers.
2. Ira Williams. The Thermal Properties of Rubber and Rubber Pigments.
3. H. W. Greider. Physical Properties of Rubber Compounded with Light Magnesium Carbonate. (Lantern.)
4. Norman A. Shepard and Stanley Krall. The Relation between Chemical and Physical State of Cure of Rubber Vulcanized in the Presence of Certain Organic Accelerators. (Lantern.)
5. W. B. Wiegand. Physical Testing Graphs. (Lantern.)
6. Rubber Division Methods for Rubber Analysis Report of Committee, and Discussion.
7. Organic Accelerators. Symposium. Specification Standards and Testing, including Both Chemical and Physical Tests in Compounds.

SUGAR CHEMISTRY DIVISION

S. J. Osborn, *Chairman* Frederick Bates, *Secretary*

1. C. A. Browne. The Moisture Absorptive Power of Different Sugars and Carbohydrates.
2. W. D. Horne. Sugar Purity Determinations.
3. C. E. G. Porst and M. Moskowitz. Plastometer Tests on Alkaline Thin Boiling Cornstarches.
4. H. T. Ruff and J. R. Withrow. The Determination of Gums in Raw Sugars.
5. O. A. Sjostrom. The Determination of the pH Value of Commercial Glucose as a Substitute for the Candy Test.
6. B. B. Ross. Some Notes on the Determination of Reducing Sugars.
7. W. P. Valentine. An Improved Precision Refractometer for the Sugar Industry.
8. M. H. Wiley. The Observance of Mutarotation in the Polarization of Raw Cane Sugar.
9. F. W. Zerban. Note on the Color Range of Cane Sirups and Molasses.
10. C. E. Coates. Manufacture of Plantation Standard Granulated Sugar with and without Activated Char.
11. P. M. Horton. The Decolorizing Power of Bone Char. (Preliminary Report.)
12. W. D. Horne. Color and Ash Absorption by Boneblack and Decolorizing Carbons.
13. J. F. Brewster and W. G. Raines, Jr. Control of Reaction in Sugarhouse (and Refinery) Liquors. (Lantern.)
14. J. F. Brewster and W. G. Raines, Jr. The Precipitate Formed in Sugarhouse Sirups. (Lantern.)
15. H. H. Peters and F. P. Phelps. Modifications in the Use and Application of the Hess-Ives Tint Photometer. (Lantern.)
16. W. B. Newkirk and H. H. Peters. Color Values of High-Grade Sugars. (Lantern.)
17. E. P. Clark. Note on a Laboratory Vacuum Still. (Lantern.)
18. R. S. Black. The Preparation of Adonitol.

WATER, SEWAGE AND SANITATION DIVISION

A. M. Buswell, *Chairman* W. W Skinner, *Secretary*

1. Edward Bartow, M. E. Flentje and W. U. Gallaher. The Effect of Temperature on the Rate of Reaction in Water Softening by the Lime-Soda Ash Method.
2. A. M. Buswell. Observations on the Mechanism of Iron Removal.

3. J. W. Sale. **Specific Gravity of Mineral Waters by Calculation.**
4. W. W. Skinner, C. H. Badger and J. W. Sale. **Bottled Mineral Waters of Unusual Composition.**
5. W. F. Monfort. **Two Instances in Which Acute Troubles Were Explained by Means of the pH Determination.**
6. W. D. Hatfield. **Data on the Application of pH Value to the Operation of Filtration Plants.**
7. A. M. Buswell. **Formulation of Equilibria in the Coagulating Basin.**
8. A. M. Buswell. **Report of Committee on Standard Methods of Analysis.**

Topic for Discussion: **Specifications for Lime for Water Treatment.**

The Chemical Exposition

The Eighth National Exposition of Chemical Industries will be held this year in the Grand Central Palace, New York, during the week of September 11 to 16, inclusive. It will follow immediately upon the Fall Meeting of the American Chemical Society. The early date will give college and university men an opportunity to see the exhibits before the beginning of the college year. There is much in this coming Exposition to interest university men. Each floor in the Exposition has exhibits of laboratory apparatus, and one floor has a considerable group of this type of equipment. Many new pieces of apparatus, new chemical compounds, and other material and instruments will be found here.

The interests for industrial chemistry in the Exposition are wide and varied: from raw materials in minerals, ores, manufacturing crudes or by-products, through the range of machinery, apparatus and equipment and instruments for control, precision, recording, gaging and measuring, and a thousand other items used in converting the raw materials into the finished products. The finished products themselves, whether they be organic, inorganic, solid, liquid, gaseous, or of any other form, are all to be there. Many new things upon which manufacturers were working when the war ended and which have been more leisurely perfected since will be shown for the first time. Industrial progress continually calls for greater advancement and perfection in manufacture, and each year sees many notable improvements upon the exhibits in the Exposition. Counting only these, the time of technical and business men is well spent in inquiring into the exhibits. One exhibitor, who for the past few years has been devoting time to the perfection of a new form of apparatus, said the other day that it is now when men have time to spare for consideration of these things that he expects a considerably larger and more interested attendance in his booth. "When the plants are idle as they are now, the most progressive companies are examining into our apparatus, and a remarkable thing is that we are making some installations in plants which are now closed, so that when they begin work they will be in better position than ever and have an advantage in taking this opportunity to prepare to reduce their costs for the future. I'm looking for many more such openings through our exhibit and with considerable enthusiasm for the entire Exposition."

The managers report that three full floors of the Grand Central Palace are already taken for the Exposition and a part of a fourth. They expect all space will be engaged before the opening date. Already, 303 exhibitors have contracted for space.

The Exposition will contain two interesting special sections: one upon the subject of fuel economy, where exhibits intended for the more efficient use of fuel, its combustion, distribution, or control will be made. The other will deal with shipping containers, including the container itself, whether of metal, wood, fiber, paper, glass or in cooperage products of slack and tight barrels, tanks and towers, and with machinery for packaging, labeling, handling, and conveying the packaged material and marking it ready for final shipment.

Work upon the program has not yet been actively undertaken but it may be expected to compare more than favorably with the high standards of the preceding Expositions. The management have returned to the Grand Central Palace with their offices, and all inquiries should be directed there.

Plan Now for Pittsburgh in September!

Convention dates, September 5 to 9, 1922

We are actively preparing for the coming of our guests, having special regard to arrangements for comfortable quarters at minimum cost, convenient and suitable meeting places, cordial welcome and interesting entertainment, excellent technical program and profitable excursions to glass works, enameling plants, iron and steel plants of all kinds, zinc and sulfuric acid plants, coal mines, and by-product coke plants.

Dormitory accommodation at a maximum rate of $1.50 per day will be available for 350 men and 50 ladies. Hotel space will be ample if arranged for well in advance.

The great Music Hall of the Carnegie Institute has been placed at our disposal for the opening meeting and for the public meeting. We hope to combine registration and personal welcome before the opening meeting, Wednesday morning.

The meetings, except that of the Council, will be held in the neighborhood of the Carnegie Institute.

The ladies will be especially well entertained. Details will be announced later.

We hope that the attendance at the meeting will break all records.

James Otis Handy, *Chairman*

S. O. C. M. A. Officers

The Synthetic Organic Chemical Manufacturers Association of the United States held its first Annual Meeting at the Hotel Pennsylvania on Friday, March 31, 1922.

Officers for the ensuing year were elected as follows:

President: Chas. H. Herty
Vice Presidents:
    Dyestuff Section, C. N. Turner, Newport Chemical Works, Passaic, N. J.
    Intermediate Section, Chas. A. Meade, E. I. du Pont de Nemours & Co., Wilmington, Del.
    Pharmaceuticals Section, Herman Seydel, Seydel Mfg. Co., Jersey City, N. J.
    Fine Organic Chemicals Section, P. Schleussner, Roessler & Hasslacher Co., New York City
Treasurer: Donald McKesson, McKesson & Robbins, New York City
Board of Governors:
    Vice Presidents, *ex officio*
    August Merz, Heller & Merz, Newark, N. J.
    F. P. Summers, Noil Chemical & Color Works, New York City
    S. Iserman, Chemical Co. of America, New York City
    F. E. Signer, Butterworth-Judson Corp., New York City
    W. T. Cashman, Grasselli Chemical Co., Cleveland, Ohio
    S. W. Wilder, Merrimac Chemical Co., Boston, Mass.
    A. S. Burdick, Abbott Laboratories, Chicago, Ill.
    Donald McKesson, McKesson & Robbins, New York City
    F. L. McCartney, Monsanto Chemical Works, St. Louis, Mo.
    James T. Pardee, Dow Chemical Co., Midland, Mich.
    Chas. H. Herty, *ex officio*

The Carbon Electrode

The National Carbon Company has issued a little booklet of 79 pages dealing with the carbon electrode. In addition to an account of the history and a description of the manufacture of carbon electrodes, the booklet contains electric furnace diagrams, standard electrode data, physical and mechanical properties of carbon, and various formulas and tables which should prove of value to the users of electric furnaces.

A. C. S. Division and Section Meetings

DIVISION OF AGRICULTURAL AND FOOD CHEMISRTY

The Division of Agricultural and Food Chemistry held two long sessions on Wednesday with T. J. Bryan, *Chairman*, presiding. Of the 21 papers on the program all were read and discussed except three which were read by title in the absence of the authors. The papers on self-rising and bleached flours promoted very active and interesting discussion. The authors of these papers showed that flours low in gluten were being used very extensively in the South and that in some instances leavening agents were not present in proper proportions to obtain the best results. The paper by B. B. Ross on "The Occurrence and Composition of Some Alabama Phosphates" was very interesting and showed plainly that there were large and rich deposits of this phosphatic material in Alabama awaiting development. A paper by Dr. E. H. S. Bailey of Kansas on a dietary study of some state institutions showed the necessity for such investigations and that more such investigations should be made of the various institutions of several states. Mr. F. W. Robison brought out the fact that a new electric method of treating milk produces a product which is better than the pasteurized milk that is ordinarily produced.

The meeting as a whole was unusually well attended and more interest in discussion was shown than has been seen for some time. At Pittsburgh next fall the Division will devote one full session to a symposium on food fats, with Dr. David Wesson as Chairman.

C. S. Brinton, *Secretary*

DIVISION OF BIOLOGICAL CHEMISTRY

In the absence of the Chairman, Howard B. Lewis, who was unable to attend the meeting on account of sickness, Secretary J. S. Hughes presided at the meetings of the Division. During the morning session eight very interesting papers covering a wide range of subjects were presented. Of these the one presented by Atherton Seidell, in which he discussed some of his difficulties in attempting to isolate Vitamin B, was very interesting and called forth some discussion very helpful to people working in this field. At the afternoon meeting five papers were presented. Three of these were on the subject of vitamins, two by J. S. Hughes concerning the effect of feeds low in vitamins on domestic animals, the other by C. H. Hunt on Vitamin C contained in goat's milk. These papers were received with the interest always accorded the papers on this very interesting subject. One of the most interesting and timely papers of the entire meeting was that by I. K. Phelps on "The Decomposition of Food by *Bacillus botulinus*." In discussion of this subject Dr. Phelps gave a very full and interesting report of a number of cases of botulinus poisoning which had occurred recently. At the meeting in New York last fall a committee, of which Dr. A. D. Emmett was Chairman, was appointed for the purpose of devising some standard method of feeding and caring for experimental animals to be used in the study of the nutritive properties of foods. Dr. Emmett was unable to attend the meeting but submitted a report for the committee. This report states that progress has been made but as yet no definite methods can be suggested for this work. Reports at future meetings will be received on this subject.

J. S. Hughes, *Secretary*

DIVISION OF DYE CHEMISTRY

Before starting the papers the Secretary of the Division enumerated a few of the activities in which the officers of the Division had been engaged since the last meeting. In accordance with the resolution of the Division at the Rochester Meeting in the spring of 1921, the Secretary of Commerce was petitioned to supply the information on individual dye marks that had been elided from the Norton Census of Dyes because of the protest of the importers of German dyes. In accordance with this resolution the Bureau of Foreign and Domestic Commerce prepared a supplement to the Norton Census, giving this desired information. These supplements have been distributed to all registered members of the Division and also to other interested parties.

The Secretary of the Division has also been coöperating with the Society of Dyers and Colourists of Bradford, England, in the preparation of the Color Index. The Coöperation Committee of the Division had one meeting in the early winter with the Color Laboratory in Washington and the report of this visit was made to the Division.

Several men were prevented from attending and their papers were read by title. Dr. Max Phillips of the Color Laboratory in Washington read a paper by himself on "The Preparation of 7, 7′-Di(-hydroxy-isopropyl)-indigo," and he also presented a paper by Mr. H. L. Haller of the same laboratory on "The Preparation of Phenylglycine-*o*-carboxylic Acid. I—From Anthranilic Acid and Monochloroacetic Acid." Dr. E. Emmet Reid of Johns Hopkins spoke about some work which he and Mr. Waldron had been doing on azo dyes containing sulfur. Dr. Reid exhibited samples of dyeings showing that when sulfur was in a position directly bound to the benzene ring its influence was to deepen and redden the shade of azo dyes. Dr. M. T. Bogert described work which he and Dr. Meyer had done on "Experiments with Dehydrothio-*p*-toluidine and Related Compounds." Dr. Bogert announced that quite recently he had prevailed upon Columbia University to relieve him of all his work except that pertaining to dyes, intermediates, and related compounds. Dr. Jules Bébie described a number of uses for the saccharin by-product, *p*-toluenesulfonyl chloride. "The Analysis of β-Naphthylamine" by a number of different methods was described by Messrs. Henry R. Lee and D. O. Jones.

R. Norris Shreve, *Secretary*

DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY

The practice of the Division of Industrial and Engineering Chemistry of holding a symposium upon a subject of vital importance to industrial chemists is proving extremely valuable. At Birmingham the subject was "Distillation," and the interest in it was demonstrated by the fact that over one-third of the chemists present at the Convention were in attendance at the meeting. Papers giving the fundamentals underlying the subject were presented. The applied phases of the topic were also well covered. W. A. Peters, Jr., was chairman of the symposium, and he is to be highly commended for arranging such a well-balanced set of papers. Many papers were promised to him by chemists, who later found that their firms did not wish them to present papers at this time. The papers presented before the symposium will be published in the June issue of This Journal.

Many papers on the general program dealt with gases and fuels; those by Drs. Fieldner and Parr provoked considerable discussion. The tendency to draw specifications for everything was discouraged in a paper by Dr. Collins. Reliable brands often mean more than detailed specifications. Mr. Shreve's paper showed by statistics how an American potash industry, if given a brief period of protection, would become a very valuable national asset. At last a scientific attack on the subject of whitewashes has been begun, and some valuable results and conclusions were given by Mr. Fink.

At the business meeting of the Division it was unanimously voted to recommend to the Society that a Section on Gas and Fuel Chemistry be created at the Pittsburgh Meeting. Reports were read from the following committees: Lime Committee (progress reported); Standardization of Apparatus and Material Committee (progress reported); Methods of Analysis and Specifications of Commercial Soaps and Soap Products (committee presented final report which was referred to the Advisory Committee). The Acting Secretary was unanimously elected Secretary of the Division. Automatic Process Control is the subject upon which the symposium will be held at Pittsburgh.

E. M. Billings, *Secretary*

DIVISION OF ORGANIC CHEMISTRY

Of the 34 papers on the program, 29 were presented. Although the attendance was small, averaging about 30, the discussion of the papers was unusually lively. This may have been due to the fact that abstracts of all the papers had been mailed to the members about ten days before the meeting. Among the papers which aroused the most discussion, were the following: Dr. Gilman's paper on the "Preparation of the Grignard Reagent;" "Catalytic Reduction of the C-N Complex," by De Witt Neighbors, S. M. Clark, J. E. Miller, A. L. Foster and J. R. Bailey; and Dr. Hibbert's paper on "Crotonaldehyde." The regular papers of the Division were followed by a symposium with the Cellulose Division on the recent work on the constitution of starch and cellulose. Dr. Hibbert gave a very lucid discussion on recent work in this field, especially that of Helfrich. Dr. Mahood continued the discussion, giving the recent work of Haworth and Irvine on the disaccharides. He also gave at some length the work of Kurt Hess on the structure of cellulose. Dr. Hibbert called attention to the flaws in the work of Hess, as shown by the results of Freudenberg, Karrer, and others. He also gave a discussion of his own cyclic formula for the nucleus of cellulose, pointing out its strong points and its weaknesses. The small number of chemists registered in the Organic Division does not adequately represent the organic chemists of the country. The Secretary will be very glad to receive suggestions for methods of reaching organic chemists and for the names and addresses of any chemists likely to be interested in the work of the Division. Such suggestions and names should be sent to the Secretary, Northwestern University, Evanston, Ill.

FRANK C. WHITMORE, *Secretary*

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DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

The Division held three very interesting sessions, at which 26 papers were presented. They joined with the Division of Industrial and Engineering Chemistry for their symposium on distillation Wednesday morning. At the business meeting of the Division, after considerable discussion of possible methods of arranging the program, it was voted that the arrangement be left to the discretion of the Secretary, with instructions to place related papers together on the program, regardless of their priority of receipt or, within reason, of the number of papers offered by one individual.

Professor Bingham gave the following report, as Chairman of an informal committee nominated this year to consider the perpetuation of the *Journal of Physical Chemistry:*

> WHEREAS, arrangements have been made whereby the *Journal of Physical Chemistry* will be continued and probably internationalized, and
>
> WHEREAS, the continuation of the *Journal of Physical Chemistry* is of importance to all chemists, especially those interested in special fields of physical chemistry, such as colloid chemistry, adsorption, surface catalysis, capillary chemistry, etc., as a medium of more extended publication of research than can be printed with the present funds of the SOCIETY in the *Journal of the American Chemical Society*, and
>
> WHEREAS, it has been suggested that the *Journal of Physical Chemistry* be published under the auspices and direction of the AMERICAN CHEMICAL SOCIETY and The Chemical Society (London), and
>
> WHEREAS, it is desirable that all scientific chemical activity in America, so far as possible, shall be centered within the AMERICAN CHEMICAL SOCIETY,
>
> *Therefore be it Resolved*, that the Division of Physical and Inorganic Chemistry recommend to the Council that the officers of the SOCIETY be instructed to correspond with The Chemical Society, and to arrange, if possible, for the appointment of an editor and a board of editors and, if necessary, a board of control, by the AMERICAN CHEMICAL SOCIETY alone, or in conjunction with The Chemical Society, to take over and direct the future of the *Journal of Physical Chemistry*, if it can be done without expense to The Chemical Society.
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> *Be it Further Resolved*, that an arrangement be made with the Board of Control of the *Journal of Physical Chemistry* whereby members of the AMERICAN CHEMICAL SOCIETY and of The Chemical Society, if the latter society jointly acts with the AMERICAN CHEMICAL SOCIETY in the matter, may receive a reduced rate of subscription over that extended to nonmembers of these societies.

After considerable discussion it was voted that (subject to the written approval of the report by the majority of the members of the special committee) the Division should recommend to the Council that the SOCIETY adopt the plan outlined in the committee report.

Among the papers which attracted special interest were those of Sosman and of Wherry bearing on the structure of solid crystals; of Franklin on ammono-nitric acid. Edgar and Schuyler gave interesting data on the equilibrium in the vapor phase between acetic acid, alcohol, and ethyl acetate which cleared up certain apparent contradictions in previously reported studies on the catalysis of this reaction in the vapor phase.

W. A. Noyes and J. T. Wilson reported accurate data on the ionization and general behavior of hypochlorous acid, bearing upon the possible existence of a positive chlorine ion.

R. E. WILSON, *Secretary*

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DIVISION OF RUBBER CHEMISTRY

R. P. Dinsmore presented a paper on "Internal Mixers" which summed up his experience. He left the audience much undecided as to the advisability of the general application of this type of mixer. Ira Williams, in his paper on "The Thermal Properties of Rubber and Rubber Pigments," showed very careful work on diffusivities and conductivities of rubber, fabric, and pigments.

H. W. Greider showed that magnesium carbonate ranks near zinc oxide and carbon black as a filler, nine volumes to one hundred volumes of rubber being the optimum amount and also the maximum advisable in most cases. High set restricts its use. The paper of Norman A. Shepard and Stanley Krall covered experiments with common organic accelerators. With a compound consisting of 48 parts of rubber, 48 of zinc oxide, and 3 of sulfur they secured equivalent cures at 60 min. at 141° C. as determined by coinciding stress-strain curves with the following parts of accelerator: 0.5 of hexamethylenetetramine; 0.25 of *p*-nitrosodimethylaniline; 0.75 of aldehyde ammonia; and 1.5 of thiocarbanilide. True coefficients of vulcanization were determined. Wide variations were found. The authors reached the conclusion that there is no relation between the coefficient of vulcanization and physical properties.

W. B. Wiegand presented standard forms and methods of plotting data. W. W. Evans announced that the rubber division methods of analysis are ready for publication and will come up for adoption at the September meeting. The Geer age test was adopted as standard.

The incorporation of chemical tests in specifications for hose, insulated wire, etc., was opposed by several members. It was the feeling of those present that specifications should be limited to physical and life tests. The present specifications are restricting development. About 35 were in attendance.

C. C. NORTH, *Acting Secretary*

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DIVISION OF SUGAR CHEMISTRY

The Division of Sugar Chemistry held its sessions on Wednesday and Thursday, S. J. Osborn, *Chairman*, presiding. The attendance showed a good representation of all important branches of the industry and even included one visitor from the Island of Mauritius, who presented a paper. Great interest was shown in the work of the Division and progress was reported on many of the problems which had been recently receiving attention at the hands of the sugar chemists and technologists. "The Manufacture of Plantation Standard Granulated Sugar with and without Activated Char" was ably summarized by Professor Coates, and other papers on the properties of boneblack and decolorizing carbons showed that the interest in this subject still continues and that there is much further work yet to be done. The measurement of color was covered by papers read by H. H. Peters, reporting investigations of himself and others at the Bureau of Standards on the fundamentals of the problem, and Dr. F. W. Zerban gave some data regarding the color range of cane sirups. Dr. C. A. Browne presented some interesting figures on the "Moisture Absorptive Power of Different Sugars and Carbohydrates," showing that some commonly held ideas needed revision. Dr. J. F. Brewster had some interesting data on "The Control of Reaction in Sugarhouse (and Refinery) Liquors" and the composition of the precipitate formed in sugarhouse sirups. Mr. W. P. Valentine described and exhibited an improved precision refractometer for the sugar industry which was favorably commented upon by those interested in refractometric determinations. The rare sugars were represented in a paper by Mr. R. S. Black on "The Preparation of Adonitol." Analytical methods were discussed in several papers, of particular interest being the case reported by M. H. Wiley on "The Observance of Mutarotation in the Polarization of Raw Cane Sugar."

S. J. OSBORN, *Chairman*

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DIVISION OF WATER, SEWAGE, AND SANITATION

While the attendance at the meeting of the Division of Water, Sewage, and Sanitation was smaller than at any meeting during recent years, there being only 26 in attendance, the interest and enthusiasm were greater than usual. The program was most interesting and the papers were fully discussed. This was especially true of the paper by Bartow, Flentje and Gallaher on "The Effect of Temperature on the Rate of Reaction in Water Softening by the Lime-Soda-Ash Method," a topic of peculiar interest to the chemist at present interested in water supplies and water treatment plants.

The paper by Hatfield on the "Application of pH Value to the Operation of Filtration Plants" was also well received and thoroughly discussed.

The Chairman, Dr. A. M. Buswell, made a full report on the activities of the committee from the AMERICAN CHEMICAL SOCIETY appointed to coöperate with a similar committee from the American Public Health Association to revise the standard methods of analysis issued by the latter association.

Owing to the extended discussion of the formal papers time was not available for consideration of the special topic for discussion, namely, Specifications for Lime for Water Treatment. Accordingly, the Division voted to defer this topic until the fall meeting.

In the afternoon the Division was entertained by an automobile trip to the Birmingham Pumping and Filtration Plant, located about ten miles northeast of the city. Visitors to the plant freely expressed the opinion that it was one of the best arranged and best equipped plants that they had ever inspected.

W. W. SKINNER, *Secretary*

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SECTION OF CELLULOSE CHEMISTRY

The attendance at the meetings of the Section was very good, and the full discussion of the papers presented indicated unusual interest in the subject of cellulose chemistry. After some revision, the report of the Standard Cellulose Committee outlining a method for the preparation of a standard cotton cellulose for research purposes was adopted. The Committee on Analytical Methods reported progress and announced that its final report would be ready for the next meeting. The Viscosity Measurement Committee reported that further study of the falling ball method in comparison with other methods was being made and that a report would be submitted at Pittsburgh. The report of the Treasurer, showing a substantial cash balance on hand, was adopted. The papers covering the report of work done at the Forest Products Laboratory showed that nine additional species of American woods had been analyzed. The results of this series of investigations as a whole show that the woods fall into two classes on a basis of their constituent groups, which correspond to the botanical divisions, broadleafed trees and conifers.

A study of the products obtained by the hydrolysis of spruce cellulose with dilute sulfuric acid established the very important fact that this cellulose does not yield glucose exclusively on hydrolysis, but a mixture of glucose and mannose.

The investigation of sugar formation in a sulfite digester shows that sugar production is most rapid between the seventh and ninth hours of the cook, during which time the chips are disintegrated. The sugar formation increases with increase of the free sulfur dioxide content of the cooking liquor. The maximum formation of sugar with minimum loss of pulp occurs at about the twelfth hour. Studies on the formation of galactose obtained by the acid hydrolysis of western larch wood have demonstrated that this sugar, which, under the conditions hitherto employed, had not been fermented, can be converted into alcohol by adding an autolyzed yeast nutrient to the fermentation liquor and maintaining a low acidity during fermentation. This procedure increases the yield of ethyl alcohol from western larch by approximately 100 per cent.

Further comparative tests on the procedures of Schorger and of Sieber and Walter for the determination of cellulose by chlorination show that the lower yields obtained by the latter are due to too concentrated a stream of chlorine and that comparable values may be obtained by diluting the chlorine with an equal volume of air in the latter procedure.

Progress has been made, as indicated by the papers on the subject, in the synthesis of acetal derivatives and of simple bodies of the polysaccharide type which promise to throw much light on the chemistry of cellulose.

The symposium on the production of cheap cattle foods by acid or alkaline treatment of waste cellulosic materials showed considerable advance in this field. Sawdust, hydrolyzed with 1.8 per cent sulfuric acid, yields a product which feeding experiments show is a good substitute for barley or corn in a grain ration. Straw with an edible content of 8 to 10 per cent can be made to yield a feed with an edible content of 56 per cent by the simple treatment of heating it in chopped form with 8 per cent of its weight of a 1 per cent soda ash solution.

S. A. MAHOOD, *Secretary pro tem*

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SECTION OF CHEMICAL EDUCATION

The Section on Chemical Education opened sharply at 9:30 on Wednesday morning with Dr. Edgar F. Smith as Chairman. After a few remarks by Dr. Bingham on the important role which a teacher may play in the extension of the metric system, the morning was given over to "An Ideal First Year Course in Chemistry." A paper by Wilhelm Segerblom on high school chemistry and a discussion of college chemistry by William McPherson started a very interesting meeting. Many participated in the discussion, with the result that the Section purposed to do something if possible to bring about a better correlation of high school and college chemistry.

The Wednesday afternoon meeting was opened by an interesting talk by W. K. Lewis on "Studying Chemical Engineering by the Unit-Operation Method." The advantages and disadvantages were clearly shown, with the result that the former far outweighed the latter. The paper by Dr. Daniel and the interesting remarks by Drs. Desha and Williamson, Jr., raised some very healthy discussion in regard to chemical engineering education. Two outstanding conclusions were: (1) the courses offered by different universities in chemical engineering are far from uniform, and (2) the chemical engineer needs a broader education before he begins to specialize.

On Thursday morning the meeting was opened by Dr. Bogert. He described some of the new organic courses which are now available at Columbia University. Dr. Swan spoke next on "A Book and a Battery." His remarks were extremely interesting from a historical standpoint. Dr. Cuno showed how the teaching of organic chemistry might be simplified and forcefully taught by means of charts. Dr. Webb gave some of his findings on standard tests with the purpose of sounding out the chemists as to their desires in the extension of standardization work in chemistry. From encouragement received at the meeting, he will continue his work and report again at some future meeting of the Section. Dr. Montgomery gave his experience in teaching unified courses in chemistry. Dr. Mahin's paper on "Science or Athletics?" brought forth a flood of discussion, and as a result a motion was passed to ask for the paper's release from the SOCIETY, in order that it might be published in some paper where it would reach the hands of the most teachers.

NEIL E. GORDON, *Secretary*

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SECTION OF HISTORY OF CHEMISTRY

The meeting of the Section on the History of Chemistry was attended by over one hundred chemists. A large amount of interest was manifested in the program, which was devoted principally to a discussion of the early chemists and chemical industries of America, more particularly of those in the South. President Edgar F. Smith opened the program with an entertaining address upon the life and work of Dr. Thomas Cooper who for many years was professor of chemistry at the South Carolina College at Columbia.

Rev. George L. Coyle read a paper upon the work of Father Athanasius Kircher, a seventeenth century scientist distinguished for his opposition to alchemy and the many-sidedness of his attainments. The paper of Ralph H. McKee upon "Some Photographic Reminiscences of the Priestley Centennial of 1874" was presented with photographs by the Chairman. A letter from S. P. Sharples was read describing the Centennial Meeting which resulted afterwards in the formation of the AMERICAN CHEMICAL SOCIETY. John N. Swan exhibited one of the early electric batteries used by Sir Humphrey Davy and spoke of Davy's work upon the electrolysis of the metals of the alkalies and alkaline earths. J. A. Gunton showed an early chemical slide rule and gave an account of its origin and use. William McPherson spoke entertainingly upon reminiscences of celebrated Italian chemists. C. A. Browne read a paper on sources of information upon early chemistry and chemical industries in America. He mentioned as among the earliest pieces of chemical work performed in America the assay of silver ores by Spanish explorers in Arizona in 1598. B. B. Ross spoke upon the early indigo, sugar, naval stores, and other chemical industries of the South. The first plant for artificial refrigeration in the United States was established by Dr. John Gorrie of Apalachicola, Florida (patented 1850). Dr. Ross spoke also of the early work of Prof. John Darby at the East Alabama College, now the Alabama Polytechnic Institute, and exhibited a Berzelius alcohol lamp used by him. A paper by Elton R. Darling described the early salt industry of the Ohio River and Kanawha Valley. In the absence of Dr. Eugene A. Smith his paper upon early southern chemists was presented by Prof. S. J. Lloyd of the University of Alabama. The various papers and addresses were supplemented by exhibits of rare books, letters, photographs, and apparatus. President Smith in summing up the work of the Section made a strong plea for historical chemical research in America in the different sections of the United States.

C. A. BROWNE, *Chairman*

SECTION OF PETROLEUM CHEMISTRY

The sessions of the Section were well attended in proportion to the size of the meeting and were marked by interested and pointed discussion of the papers presented, as well as of the question of policy and business, which came up for attention. Theoretical aspects of petroleum science were considered in papers on the viscosity of fluids, presented, respectively, by W. H. Herschel and W. H. Fulweiler, and in one paper on surface tension of oils by C. K. Francis. The practical sides of oil technology were considered in R. R. Matthews' paper on the corrosion of refining equipment, in the discussion of volume changes in petroleum products by A. P. Bjerregaard, and in a paper on natural gasoline recovery by F. M. Seibert and F. E. Hosmer. Petroleum education was discussed by Edwin DeBarr and F. W. Padgett.

The discussion of policy of the Section in formulating divisional by-laws brought out a resolution that, while every phase of petroleum chemistry should be open to the Section, it would be advisable to avoid the writing of specifications and the formulation of standard methods of testing. In the Conference on the Promotion of Research on Petroleum, in which the American Petroleum Institute was represented by Dr. Van H. Manning, an endorsement was made of the research objects of the Petroleum Institute, as described by Dr. Manning, and it was decided to appoint a committee, which should include representatives of the National Bureaus of Standards and Mines, to coöperate vigorously with Dr. Manning in promoting a joint research program on the "Chemistry and Chemical Technology of Petroleum."

W. A. Gruse, *Secretary*

A. C. S. Committee Reports

REPORT OF COMMITTEE ON EMPLOYMENT BUREAU

Your Committee appointed to consider the taking over of the Employment Bureau of the Chemists' Club by the American Chemical Society or to establish a bureau of its own to replace this organization, begs leave to submit the following report.

Your Committee appreciates the importance of the whole subject of employment. There can be no question as to the desirability of the establishment of some adequate provision whereby the chemist and the individual desiring the services of the chemist may be brought together to their mutual advantage. The vital question, therefore, is what is the best arrangement for securing the desired ends. A number of plans have been proposed.

Plan A—The present Employment Bureau of the Chemists' Club may be taken over by the American Chemical Society and expanded so that it will serve the Society as a whole. Such a bureau, if established, would have to be either (1) a free employment agency, or (2) a paid employment agency.

The vital question in connection with the free employment agency plan is the financial one. What will the plan cost the Society? Some idea can be obtained from the experiences of the Bureau of the Chemists' Club. This Bureau was incorporated in 1913 and has registered since that time 7356 different individuals and has filled 1955 positions. Its expenditures in its early years were about $7000, increasing with the larger patronage to approximately $10,500 for the year ending May 1921. It is probable that if the Bureau were increased to serve the whole Society these expenditures would at least be doubled. The Federated American Engineering Societies have a budget of $17,900 for the present year for their Employment Agency. The American Association of Engineers, with a highly organized agency and a number of branches, spends about $30,000 for a similar purpose. The adoption of this plan would therefore necessitate an expenditure on the part of the Society of at least from $15,000 to $20,000 per annum.

The Society, on the other hand, may adopt the paid agency plan. If this is done, however, it will be practically necessary to form a separate corporation. Otherwise, the Society will become subject to a number of taxes, including both national and state income taxes.

Plan B—The Society may establish a separate corporation and run a paid agency. Judging from the experience of the Chemists' Club and teachers' agencies, it would seem a probable assumption that such an agency could be made self-supporting unless in times of great depression like the present. The Bureau of the Chemists' Club has been self-supporting until the present business depression.

Plan C—The various Local Sections may finance and operate employment bureaus for their own members as is done in a few cases at present.

In this plan the Society would have no financial interest whatever. Each Local Section would finance its own agency in whatever way it desired. One advantage of this plan would be that each agency would serve a more or less restricted community and hence could know its patrons better and be in a better position to recommend the right man for the right place. On the other hand, it has a disadvantage in that there are a number of members of the Society who belong to no Local Section and hence would be left out in such a plan.

Plan D—The various Local Sections may operate their own bureaus as proposed in Plan C, but in addition there may be operated a central office, limited in its scope but able to serve the members of the Society who do not belong to any Local Section, and in a general way to coöperate with the bureaus of the Local Sections. Such a central office could be located preferably at Washington, under the supervision of the Secretary of the Society or the Editor of the *Journal of Industrial and Engineering Chemistry*. The expense of such a plan would be a nominal one, certainly not to exceed $4000 or $5000.

Plan E—The Society may unite with the Federated American Engineering Societies in the establishment of a general employment bureau.

Believing it to be outside its jurisdiction, the Committee has made no effort to ascertain whether or not the Society would be welcomed as a member of the Employment Bureau of the Federated Societies.

Plan F—The Society might interest appropriate individuals in the plan of starting a paid employment bureau for chemists to be operated for profit on the same general plan as a teachers' agency. In operation of this plan the Society would have no part except a sympathetic interest.

This plan would probably be acceptable to the members of the Society (and the number seems to be large) who believe that the Society ought to have nothing whatever to do with the employment bureaus, that the average individual who secures employment through an agency is apt to be disappointed, and that on the whole the Society would make more enemies than friends by maintaining an employment bureau.

The question submitted to the Committee is one that is of such vital interest and also one concerning which there are such strong and divergent opinions that the Committee has thought it unwise at this time to make any final definite recommendations but submits the following for general consideration:

1—That the Council be asked to consider the various plans proposed or any additional plans not listed above with a view to finding out which one of these plans, if any, is desirable.

2—That, after a full consideration by the Council, this report, together with such instructions as the Council may care to give, be referred back to the Committee or to a new committee for further consideration and report at the next meeting of the Society.

Wm. McPherson, *Chairman*

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REPORT OF COMMITTEE ON OCCUPATIONAL DISEASES IN THE CHEMICAL TRADES

This year the Committee has been unfortunate in the loss of its Chairman, and in consequence thereof has found itself, when confronted with the problem of preparing the report, in a chaotic frame of mind.

The past year has brought us face to face again with certain occurrences and facts in the field of occupational diseases and industries, and especially with reference to their causation and prevention.

The letter files of the Committee have grown considerably, and this can be taken as an indication that the chemical and allied industries consider more seriously occupational hazards and diseases as truly economic items.

The enlightened viewpoint is the result of many factors working in the same direction, some for the protection of the employees and others for the protection of employers.

In this spirit of better progress a greater tendency prevails, on the part of the industries, to employ more physicians and hygienists, and many concerns who heretofore regarded sanitarians as a luxury not to be indulged in now find it a valuable arrangement

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The time has come when we are realizing that something more is necessary in this work than the sole qualification of being a doctor of medicine. We are now in the age of prevention and not in one of an expectant industrial pathology. Consequently we must expect our physicians and others trained in industrial hygiene to be basically trained for this kind of work. We are also conscious of the fact that each industry presents its individual hygienic problems which can be worked out only when the physician is actually a member of the force in the particular chemical factory.

* * * * *

Our hygienists must further be able to think of how the particular chemical will affect the human body, of the means at hand for rendering first aid, and, in the case of the physician, of after-treatment for casualty cases.

A spirit of coöperation must always obtain between the superintending chemist and engineer and the industrial hygienist and physician in order to get the best results. Each possesses special knowledge which, when properly associated, will tend to keep industrial hazards down to a minimum.

To-day, various universities and colleges offer courses in public health and industrial hygiene. * * * * * Some of the courses are intended for persons who do not aspire to the degree of doctor of medicine, and lead to the bachelor's degree or a higher collegiate degree, or to the doctorate in public health or a similar qualification. Other courses are open only to medical undergraduates and are counted toward the partial fulfilment of the requirements of the doctorate in medicine, or may be taken by graduates in medicine, with other work, as a course leading to a certificate or to a degree in public health. The chemical manufacturer can select a person skilled in preventive medicine or one who has the added qualification of treating injuries and diseases as they arise.

Many concerns do not employ a full-time hygienist or physician, believing it an economic waste. An arrangement of this kind, while often remunerative for the physician, is very unsatisfactory from the standpoint of industrial hygiene. * * * * * The part-time physician has no time for constructive thinking, particularly when he is chiefly engaged in an extensive outside practice.

Another step in the right direction would be to include a set of lectures on industrial hygiene in every course in chemical engineering. This, we believe, would go far toward removing some of the more flagrant, and sometimes easily removable, conditions in existence. By this we do not mean that the chemist or chemical engineer should function as a hygienist, but the knowledge gained would certainly increase his scope of view and avoid many errors and misunderstandings which now occur.

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Making careful functional examinations of the hearts of employees is emphasized by C. Phipps [*J. Am. Med. Assoc.*, **78** (1922), 562] on the basis of his findings of 650 persons for the Massachusetts Industrial Accident Board in the Workmen's Compensation Act. Out of this number 231 showed abnormal heart conditions.

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Defective vision among industrial workers, from the viewpoint of economic loss to the respective industries, is discussed by McCord and Lyle [*J. Am. Med. Assoc.*, **78** (1922), 606] on the basis of observations made in a plant engaged in the manufacture of cotton braids.

We often meet with men in chemical plants who foster the belief that wearing glasses for correcting errors of vision constitutes an admission of incapacity to conduct the tasks assigned. "The industrial physician in his dual function of serving employee and employer advances the interests of each through the careful supervision of the eyesight of all workers."

Gassing of the eyes, frequently observed among still cleaners in oil refineries, causes a blinding, painful inflammation of the conjunctiva and is said to be due to sulfur compounds in the oils. The practice of workmen in applying raw potato juice or any other poultice to the eyes in such cases is deplored by the *Journal of the American Medical Association* [**76** (1921), 1031]. G. M. S., in the same *Journal*, finds the instillation of a 1 per cent solution of holocaine and the greasing of the lids of value. * * * * *

Carbon monoxide, according to Wilmer [*Am. J. Opthalmology*, **4**, 73], causes ocular paralysis, heminaopsia (blindness of one-half of the visual field, affecting one or both eyes), and inflammation and degeneration of the optic nerve. The treatment resolves itself into remedies suggested by the various symptoms, and especially prophylaxis and hygiene.

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Detailed directions are given for the treatment of acid and alkali burns by Smith [*Modern Medicine*, **3** (1921), 232]. The strong caustics, as "sulfuric acid, nitric acid, potash, chloride of antimony, chloride of zinc, acid nitrate of mercury, bromine, chromic acid, lime and (hot iron)," are discussed.

A report on an outbreak of zinc chloride poisoning among the workers in a wood preserving industry, made by McCord and Kilker [*J. Am. Med. Assoc.*, **76** (1921), 422], again emphasizes the need of a little foresight in preventing local lesions due to handling chemicals, etc. * * * * *

Three other types of lesions were observed: a tar dermatitis (2 cases), attributable in part to preparations used in cleaning up, benzene, light and heavy oils from coal-tar distillation; tar acne, present in varying degrees in all the employees examined, and probably due to a collection of tarry matter in the hair follicles and occurring especially on the forearms; tar cancer, or a condition suggesting it, which was found in two cases. The quick disappearance of the lesions suggests caution in the pronouncement of cases as tar cancer. Deelmann [*Nederlandsch Tijdschrift Geneeskunde*, **2**, No. 20, 2395; abst. *J. Am. Med. Assoc.*, **78** (1922), 696] believes tar coming from horizontal retorts more active than tar from vertical retorts, since malignant degeneration occurs sooner. Bloch and Dreifuss [*Schweiz. mediz. Wochenschr.*, **51**, No. 45, 1033] conclude the cancer-producing substance to be in a fraction which boils at over 300° C.

Under the caption "So-called Aniline Tumors of the Bladder," Alice Hamilton [*J. Ind. Hyg.*, **3** (1922), 16] calls attention to hydrogen arsenide as a possible etiologic factor, since hydrogen arsenide poisoning is admittedly present in all conditions with which the bladder tumors of aniline workers have been associated. * * * * *

An epidemic lung disease, "Schneeburg lung cancer," which is found among many workers in the cobalt mines of Saxony, is again up for discussion. Uhlig [*Arch. path. Anat. Virchow's*, **230** (1921), 76] mentions how common it is to find men in the prime of life so affected and relegated to very light work. Arsenic is believed to be responsible for the condition. * * * * *

A dermatosis, called "ink poisoning" by printers, which affects those parts of the arms and hands subject to constant contact with colored inks, is known to have prevailed for many years among printers in the large printing and engraving plants. The workers believed green ink to be more irritant than the other colors. McConnel of the U. S. Public Health Service [*Pub. Health Reports*, **36**, 979] stresses the fact that all inks, irrespective of color, when removed by the brutal methods in vogue in the establishment at the time, are liable to cause an irritation which may lead to a dermatosis. * * * * *

An acute dermatitis of the face, hands, and forearms was noted among the women workers on phenol resins by Sachs [*Weiner klin. Wochschr.*, **34** (1921), 356], and many of the patients also presented symptoms of conjunctivitis and some bronchitis. Vapors of ammonia, phenol, and formaldehyde were noted in the room. The treatment given is described.

The part played by the skin in lead poisoning was investigated by Sussmann [*Arch. Hyg.*, **90**, 175], who found the main channels for absorption of lead to be the lungs and alimentary canal rather than the skin. Shie [*J. Am. Med. Assoc.*, **76** (1921), 835] makes the statement, "By far the greatest amount of lead poisoning occurs among the industrial workers," and gives the result of his investigations on more than 900 workers exposed to the lead hazard. * * * A refinement of the system of prophylaxis is necessary before the morbidity rate can be lowered.

Alice Hamilton [*J. Am. Med. Assoc.*, **78** (1922), 627] calls attention to the growing menace of benzene poisoning in American industries. Since benzene is a more powerful solvent than petroleum benzine or naphtha, for fats, gums, and resins, and is now below the latter in price, there is double temptation to use it. Perhaps the petroleum distillates will be supplanted by the coal-tar in the making of varnish, quick-drying paints, and shellacs, and in dry cleaning, if not in the making of spread rubber goods, as is done in Europe. Unless precautions are taken, severe and fatal cases of poisoning are bound to occur during the distillation of benzene and the cleaning of apparatus employed in the process. * * * * * Preventive measures are suggested, but in many cases it is a very difficult matter to instal certain necessary systems of prevention.

According to Minto and Smith [*Arch. Internal Med.*, **28**, 687], tetrachloromethane poisoning may be predicted from an examination of the blood. * * * * *

Only a passing reference can be made to the very important work on carbon monoxide poisoning reported during the past year. The literature has assumed large proportions, as can be judged from the article by Henderson [*J. Ind. Eng. Chem.*, **14** (1922), 229]; *Bulletin* **291** recently issued by the U. S. Bureau of Labor, with A. Hamilton as the author, and the survey of carbon monoxide poisoning in American steel works, metal mines and coal mines by H. S. Forbes [*J. Ind. Hyg.*, **3** (1922), 2].

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Progress has been made in the adoption of the term "methanol" for methyl or wood alcohol. Ziegler [*J. Am. Med. Assoc.*, **77** (1921), 1160; *Penn. Med. J.*, **25**, 177], among others, advocates the use of the term, and furthermore states that three factors should induce manufacturers to abolish the use of wood alcohol and substitute denatured alcohol: humanitarianism, self-interest, and practical economy.

Satisfactory casualty and morbidity statistics of the chemical and allied industries are not now available. It is obvious that a true picture of our economic losses from this source will never be obtained until a better spirit of coöperation exists between the manufacturer, the Committee, and public and private officials charged with this work.

It is a pleasure to know that the National Safety Council is taking a census of safety men in the chemical industry, as well as in other industries and in public safety work.

Owing to the usual lack of finances, the Committee was unable to coöperate properly with similar committees of other private technical and scientific organizations and in a previous report attention was directed to the imperative need to-day of an "Institute on Occupational Diseases and Hazards" to serve as a clearinghouse for information and direction in this field of endeavor. Such an institution would be of inestimable value for all connected with the chemical and associated industries. Much information could be collected from private, governmental, and educational sources, and through the institute made readily available to all.

It is recommended that the incoming committee direct some of its efforts to settling upon a tangible basis for obtaining funds for creating the institute.

The Committee also feels that much time could be saved by collecting all excerpts of articles on vocational hygiene, etc., in a special column of *Chemical Abstracts*, and by inserting cross references in other appropriate columns. We feel sure that with such an arrangement information on the subject would receive better attention.

LEWIS WILLIAM FETZER,
Chairman pro tem

REPORT OF COMMITTEE ON INDUSTRIAL ALCOHOL

Your Committee on Industrial Alcohol was appointed by President Smith soon after the Rochester Meeting last April as the result of a resolution adopted at that meeting.

On April 25, 1921, Mr. Volstead introduced a bill, H. R. 5033, in the House of Representatives which if passed would have seriously crippled the industries of the country depending upon legitimate uses of alcohol.

A telegraphic summons brought the Committee together in New York, where general resolutions in the name of the American Chemical Society were drawn up to be submitted to the Committee on Public Policy for their approval, which was granted unanimously. The Committee sought and finally obtained a hearing before the Committee on the Judiciary of the House of Representatives, to whom bill H. R. 5033 had been referred. [The resolutions of the Society which were presented to the Committee on the Judiciary at a special hearing were printed in This Journal, **13** (1921), 570.]

Strong representations were made by us to the Committee on the Judiciary that nothing should be done to hamper or restrict the nonbeverage use of alcohol in the industries. Our Committee received able assistance at this hearing from Secretary Parsons and other members of the Society and took advantage of the services of representatives of industries having allied interests.

Because of the strong and valid objections raised against bill H. R. 5033 it was withdrawn by the Committee on the Judiciary, it having become apparent that it would not be easy to pass it. On June 1 they substituted in its place a new bill, H. R. 6752, which though less objectionable than the first would nevertheless have put unnecessary burdens and restrictions on industries depending on alcohol. An attempt was made to pass this bill without hearings or chance of offering valid objections. The request for summary action on this bill caused it to be referred to the House Committee on Rules. This committee granted us a hearing, and after considering our objections and those of other opponents of the bill, agreed with our contention that the bill if passed would have been unconstitutional and they refused to grant the special rule in its favor. A new bill, H. R. 7294, was then introduced, practically free from features objectionable to the industries, but the author of the former bills succeeded on the floor of the House in amending it in a manner that made it objectionable.

During all this time strong influences that were unmindful and inconsiderate of the rights and needs of industries were seeking through quick moves and irregular procedure to advance their special interests and where possible they sought to avoid public hearings that would give an opportunity for voicing valid objections. This made it necessary for our Committee to be ever on the alert. We were frequently put in the position where it was necessary to decide quickly and act without delay. Our position might have been likened to the man who, seeing the start of a fire, grabbed a pail of water and put it out, instead of letting the building burn down while seeking to learn if he was authorized to take the steps he did.

Bill H. R. 7294 which was originally introduced to prevent the prescription of beer for medicinal purposes was at first amended in a manner that was somewhat inimical to the industrial users of alcohol. It was later amended in the Senate so that when it finally became a law in November 1921 it was not hostile to industrial alcohol.

We have not considered the merits of prohibition as a committee, either for or against. The eighteenth amendment is very specific in its purpose and in the authority which it grants, and the National Prohibition Act expressly states that it is "an Act to prohibit intoxicating beverages, and to regulate the manufacture, production, use, and sale of high-proof spirits for other than beverage purposes, and to insure an ample supply of alcohol and promote its use in scientific research and in the development of fuel, dye, and other lawful industries."

This being the intent of the Constitution and of existing law, the Committee on Industrial Alcohol has felt that its duties were clearly defined. If we were to be of any use as a committee we could not sit idly by and see unnecessary and burdensome restrictions put upon the industries. This is a matter that we refused to compromise on. We were either right or wrong and we have used every effort to be on the side of right, and not to take sides in any doubtful matter.

Some of the legislation which was strongly urged would have put industries at the mercy of one man who would have been clothed at the same time with powers legislative, executive, and judicial. The manufacturer was put in the position that his business depending on the legitimate use of alcohol might be absolutely destroyed. A mere refusal to act, or neglect on the part of the Commissioner, would have sufficed to accomplish this result.

Industry is not responsible for the diversion of alcohol to illegitimate purposes and it has been repeatedly brought out that most violations have been due to the promiscuous granting of permits, and in many cases to corruption in the ranks of prohibition enforcement officers and to a neglect to carry out existing law.

We are credibly informed that a very general sentiment has been established in the minds of congressmen, largely due to our efforts, that nothing shall be done to injure industry in advancing prohibition enforcement.

Failing at gaining absolute power over industries through legislation, certain over-zealous persons are suggesting and seeking at this very time to accomplish their aim through arbitrary regulations.

Our attitude has at all times been helpful to those who respect the law, and we realize that every violation of the National Prohibition Act makes it harder for those who are respecting the law.

Only recently we received a request from one of the leading officers of the Treasury Department interested in the control of alcohol and liquors to coöperate with them and to give suggestions that would lead to a better enforcement of the law, including that portion which provides for the use of alcohol in the industries. Our Committee has expressed a willingness so to coöperate.

In conclusion we wish to state that we believe there is good ground for the continuance of a Committee on Industrial Alcohol, we recommend that such a committee should be appointed for the coming year, and we believe that its members will have ample opportunity to be of service to the Society and to the country.

Martin H. Ittner, *Chairman*

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COMMITTEE ON PRIESTLEY MEMORIAL FUND

The Committee now offers its final report. It wishes to extend sincere thanks to the very generous contributors who made possible the fund with which to procure a suitable portrait of Joseph Priestley and to guarantee the cost of the die to be used in casting the Priestley Medal.

The portrait, as is probably known to everyone, is placed in the National Museum at Washington.

The die for the Medal is in the hands of Dr. John E. Teeple, Treasurer of the Society, to whom all residual monies have been paid.

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To the Committee it seems important that a record should be had of all who participated in making these undertakings possible. The names of the donors are, therefore, submitted, the amounts of their several contributions being withheld.

Charles F. Chandler
Charles Baskerville
George F. Kunz
George J. Pickel
Charles H. LaWall
H. H. Bartlett
Dean Marion Talbot
Alexander Smith
J. V. V. Boraem
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Penobscot Chemical Fibre Co.
Sowers Mfg. Co.
Herold China & Pottery Co.
Ralph E. Meyers
Otto Behrend
Gregory P. Baxter
C. A. Browne
Fred Rosengarten

The Committee would recommend to the Council the following rules to be observed in the award of the Priestley Medal:

1—The Medal shall be known as the Priestley Medal, and shall be awarded every three years for distinguished services to chemistry.

2—The Committee of Award shall consist of the President of the American Chemical Society, his immediate predecessor in office, the Secretary and Treasurer of the Society, and the Editors-in-Chief of the Journals of the Society.

3—The Medal may be awarded not only to members of the Society, but to nonmembers, and to representatives of any nation, without regard to sex.

4—The Medal shall not be awarded more than once to the same individual.

5—The recipient of the Priestley Medal may be invited to deliver an address at one of the general meetings of the American Chemical Society, as may be determined by the Committee of Award.

The Committee further recommends that the first award shall be made at the General Meeting of the American Chemical Society in September 1922.

Edgar F. Smith, *Chairman*

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REPORT OF COMMITTEE ON SUPERVISION OF CHEMICAL ENGINEERING CATALOG

The sixth edition of the *Chemical Engineering Catalog* was ready for distribution during the week of the Chemical Exposition in New York in September 1921. The book went forward systematically thereafter, the entire distribution being effected by January 1, 1922.

The introduction of a fee of $2.00 a year for the use of the *Catalog*, which was introduced in 1920, proved to be a very effective means of distributing the catalog, as it eliminated waste of copies and improved the character of the mailing list; it did not in any way diminish the demand for the *Catalog*.

Eleven thousand five hundred copies of the *Catalog* were sent out and a list has been printed, giving the name, address, and business connections of each recipient. This list is furnished to all the firms represented in the *Catalog* and its use is confined strictly to them.

In the 1921 edition there were 667 firms using space, and statistics show that there is an increasing tendency on the part of the space-users to contract for more space, in order to catalog their products properly. The total number of catalog pages in the 1921 edition is 971.

In order to lessen the weight of the book, which is becoming unwieldy, the publishers have produced it with a flexible leather cover and a much higher grade of thin paper, which makes a much improved edition.

We believe that there is a growth in the scientific value of the information given. The officers of the *Catalog* constantly refer copy of the proposed data and general information to the Committee for suggestions and criticism, and in many cases the publishers have refused profit by rejecting mere advertising and choosing, rather, more scientific copy.

The duty of the chemical engineer is to observe this particular feature and to do his share toward obtaining the desired results by encouraging space-users to present more detailed facts concerning their products.

* * * * *

Your representative attended several informal meetings of the Committee and has had a large number of informal conferences with the officers and editor of the *Catalog* and has endeavored in every possible manner to be of assistance to these gentlemen in their activities. The informal meetings are usually called to discuss principally matters of policy, as we are often called upon to assist the officers in obtaining from the manufacturers the proper data and information.

The prospects for the 1922 edition of the *Catalog* are much better than they were for 1921, when the business depression was felt. A number of firms that withdrew their space in 1921 have again applied for space in the 1922 edition, and, as stated previously, the data submitted are constantly being improved.

E. R. Weidlein, *Chairman*

....

REPORT OF COMMITTEE ON GUARANTEED REAGENTS AND STANDARD APPARATUS

The Committee has continued the work on elimination of sizes and shapes of apparatus that was described last year. A second detailed report has been prepared for publication. In this report 520 items are retained out of a total of 1246 considered by the Committee.

Elimination has been attempted without going into the question of exact dimensions. It is hoped that further recommendations may be made as to dimensions of the items retained.

W. D. Collins, *Chairman*

....

REPORT OF COMMITTEE ON STANDARD METHODS FOR THE EXAMINATION OF WATER AND SEWAGE

In coöperation with the Committee of the American Public Health Association, our Committee has completed a revision of the Standard Methods of Water Analysis, the final manuscript of which was forwarded last week to the proper authorities of the American Public Health Association for publication. When printed, it is our intention to submit a copy to the Secretary's office as a permanent record of our work.

The portions of the work assigned to members of the American Chemical Society Committee were as follows: definition of alkalinity and temporary hardness; methods for hydrogen-ion determination; methods for sewage testing; mineral analysis; standard specifications for Nessler tubes; turbidity.

It is my understanding that the title page of this revision will bear the usual inscription including the names of the coöperating societies.

The duties of the Committee for the next few months will be simply to read proof. It is therefore desirable that the present personnel be continued until the present edition is published.

A. M. Buswell, *Chairman*

....

REPORT OF METRIC SYSTEM COMMITTEE

I have the honor to submit the following report for the Committee on Metric System to coöperate with the American Metric Association, the World Trade Club, and the London and Manchester Metric Associations. We have during the year published three papers on the use of the metric system in the *Journal of Industrial and Engineering Chemistry* and also one article in *Science*. As recommended by the Council, we have also written to the colleges and universities as well as many technical firms using chemicals, urging them to purchase their chemicals in metric units; some 325 colleges have responded definitely in the affirmative, one only being opposed. Some 250 technical firms have also signified their intention of purchasing chemicals and supplies as far as practical in metric units. This work has entailed a great deal of correspondence and we have written between 5000 and 10,000 letters during the year. In this work we have had financial assistance from our Society and from the American Metric Association.

The work which we had planned for the year entailed a much larger expenditure than the money at hand and rather than hold the work back the Committee has met the expense. We have worked out a program for making this work self-supporting. We have attempted to enrol those who were coöperating with us as members of the American Metric Association, and in return the A. M. A. has agreed to give us 90 per cent of the dues received. If our policy is followed there should in time be a considerable revenue from this resource.

We have distributed some 20,000 stickers [to be affixed to letters sent to manufacturers and dealers] and have had requests for more from several sources. Their use should bring about a considerable pressure upon those firms, such as the Grasselli Chemical Company, which refuse to supply goods in metric units.

We have presented the metric cause before several bodies, such as the American Physical Society and the American Naturalists, and we have plans for a large amount of work of this sort before scientific educational bodies. The meeting on world standardization in New York was well attended and produced good results. We desire to have another meeting in Pittsburgh of considerably larger scope. We would like to have the Council give us permission to invite representatives of all the principal scientific, medical, engineering, and educational societies to meet with us at Pittsburgh to consider what steps can be taken advantageously to further the gradual adoption of the metric system in America and to investigate what the cost of the transition to the metric system may be and how the transition may be effected with the least inconvenience to the community. The question of cost is the one which is always mentioned by the opponents of the metric system. It appears probable from our experience in regard to chemicals that the argument is largely without foundation. If we could speak on this matter authoritatively after investigation, it would do much to promote the object which we have in view. Doctors and pharmacists are using metric units to a slight extent. This can be greatly increased. Some of our correspondents have begun giving talks to different bodies on the subject. We should have committees in every state to appear before our educational, scientific, and civic associations to present the metric cause. It seems to me that here is an important opportunity for leadership for our great organization.

Eugene C. Bingham, *Chairman*

Meeting of Local Section Officials

A meeting of Local Section officials took place at 4 P.M. at the Tutwiler, with W. L. Lewis presiding. Mr. E. M. Billings of the Rochester Section acted as Secretary. The following subjects were discussed:

(1) Standardization of Section By-laws. A committee consisting of the chairman and secretary was appointed to study the present Section By-laws and recommend a uniform code embodying the best features in the experience of the several sections.

(2) Relations to the National Society. The desirability of discussing National Association issues in the Local Sections, instructing and informing council-men, educating the members as to the national organization, candidates for national offices, etc., were freely discussed.

(3) Section Programs. Under this caption such matters as securing national speakers, routing prominent chemists, keeping in each section a lot of available local speakers, etc., were discussed.

Other matters considered were permanent employment bureau management work in the Sections, financing the Sections, interesting the young members, what to do with the ladies, and the desirability of educating chemists and employers to clear for positions through the college professors.

About 30 representatives of the several Local Sections were present at the two-hour session of the Section. The interest manifested demonstrated the need of and possible service through open discussions of this character.

The Chairman reported at some length on the Chicago plan of group meetings held simultaneously following the general talk of the monthly program, recommending it for consideration by the other larger sections which had not already developed something of the kind. It was generally agreed after this informal discussion, which demonstrated the proper subjects for consideration, that at the next meeting more definite progress would be made by calling in advance for the preparation of papers along some of these specific lines above suggested.

W. L. Lewis, *Chairman*

NOTES AND CORRESPONDENCE

Utrecht Meeting

Editor of the Journal of Industrial and Engineering Chemistry:

The following formal invitation has been issued to a chemical meeting at Utrecht in June:

Utrecht, March 1922

Dear Colleague:

In June of last year Professors Biilmann, Bruni, Ernst Cohen, Donnan, Victor Henri, Kruyt, van Romburgh, Schenk, Walden and Wegscheider met in conference at Utrecht, and agreed to hold there in 1922 a scientific chemical meeting, the date of which is now fixed for June 21, 22, and 23 of this year. The program will consist of several general papers, together with a number of shorter scientific communications.

It would give us very great pleasure, dear Colleague, if you would take part in this meeting.

Awaiting a reply at your earliest convenience, and with best wishes,

Yours very truly,

Ernst Cohen
H. R. Kruyt
P. van Romburgh

The following American chemists are already planning to attend the conference: Drs. Edward Bartow, W. R. Whitney, L. W. Dennis, and W. A. Noyes. Other names will probably be added to the list later.

W. A. Noyes

University of Illinois
Urbana, Ill.
March 25, 1922

Determination of Arsenic by the Distillation Method

Editor of the Journal of Industrial and Engineering Chemistry:

Messrs. J. J. T. Graham and C. M. Smith [This Journal, 14 (1922), 207] recommend hydrazine sulfate and sodium bromide in the determination of arsenic by the distillation method. Hydrazine sulfate and hydrobromic acid have been used by the writer in the laboratory of the Coniagas Reduction Co., since 1911, and about 10,000 determinations of arsenic in cobalt ores and metallurgical products have been made in the above laboratory by means of these reagents. The writer made 2 kilos of hydrazine sulfate by the elegant method of Raschig [*Ber.*, 40 (1907), 4587] during the latter part of the war, when this material could not be purchased on the open market. Among the many advantages of hydrazine sulfate over other reducing agents the writer would like to draw attention to the following points:

The introduction of large amounts of fixed salts which are liable to cause bumping during the latter stages of the distillation is avoided.

The residue from the distillation is readily available for the determination of other constituents after destroying the excess of the reagent with bromine water or hydrogen peroxide.

C. A. Knittel

45 Chaplin Ave.
St. Catherines, Ont., Canada
March 9, 1922

Some Difficulties of the Manufacturer in the United States

Editor of the Journal of Industrial and Engineering Chemistry:

The writer is technical director of the Chemisch-Pharmazeutische Fabrik ByCo., S. A., which was first organized in Los Angeles and later reorganized with increased capital in Mexico. Its products are at present standard pharmaceuticals, such as tablets, ointments, fluid extracts, etc. The manufacture of chemicals is to be taken up in the future.

I believe that there is something of general professional interest in a rather detailed account of the experience of this organization, when we struggled in vain against an ever-increasing, excessive, and extreme legislation, perhaps more pronounced in California than in any other state, which finally forced us to throw up our hands in despair and to transfer our plant to Mexico City.

In Los Angeles we conducted an analytical laboratory doing principally clinical work. Connected with the analytical laboratory was a manufacturing laboratory equipped with power machines for the manufacture of medicinal tablets, etc. Other products were cosmetics and pharmaceutical and chemical specialties. It was also planned to make flavoring extracts in collapsible tubes.

We were subjected to the following laws and permits required:

Prohibition laws, in the use of alcohol for industrial purposes, in the analytical laboratory, for cosmetic preparations, in the recovery of alcohol.

The details connected with the many intricacies of these laws, expenses, etc., referring to our plant I need not rehearse here. Suffice it to mention that the Federal office in Los Angeles refused to accept our application for the use of alcohol for certain medicinal tablets where it was essential to make the necessary granulation, without our submitting formulas and labels for such tablets, a procedure which was of course impossible because we could not foresee what formulas would be submitted to us to be made into tablets. That the alcohol was used solely as a binder and was entirely driven off on subsequent drying of the product did not change the solomonic dictum of the Federal office.

Narcotic laws, involving a permit to use narcotics for medicinal tablets, and another permit to analyze for customers preparations containing alkaloids (narcotics).

The study of the California state food and drug laws, those of the State Board of Pharmacy, Federal legislations, the filling out of the many application blanks, the monthly accounts required, the study of new amendments (added frequently) would almost require one man's time, a cost too great for a small plant.

At the time we left California, three bills were pending before the Legislature which would have added to our burden.

The first of these bills was the Economic Poison Law (disinfectants), which if passed would require a special permit to manufacture disinfectants and a yearly tax of $50 for the same, doubtless with another series of application blanks, etc.

The second referred to the labeling of flavoring extracts. According to what I have been told by a well-known color manufacturing house, the bill was intended to prohibit the use of pictorial reproductions of any fruit, as well as the names of fruits, on the label, provided the flavors were manufactured from synthetics.

The last of these bills would have been disastrous to our analytical laboratory because it would prohibit anyone but a registered physician from performing analyses of a clinical nature. An abstract of this bill was published about half a year ago in the *Journal of the American Pharmaceutical Association.*

The following species of the family of inspectors did honor us with their visits, or would have done so had we been able to obtain all the necessary permits for the manufacture of our goods (a special reception room would have been quite appropriate): boiler inspector, Board of Health inspector, safety inspector (machinery), prohibition inspector, corporation inspector, county tax assessor, scale inspector, Board of Pharmacy inspector, narcotic inspector, fire inspector, city license inspector, and *vivant sequentes.* The possible passing of the Economic Poison Law would probably have acquainted us with still another member of the family.

We do not care to express the feelings which we experienced when one of the boiler inspectors (we had a large upright gas boiler for the generation of live steam) inquired, "Which machine is the boiler," and "Is this a copper or iron boiler," and when patiently given the desired information proudly handed us his official notice, "Boiler inspected and found to be in good order."

There is a very marked contrast in the situation with which we were confronted when hopelessly striving against official meddling, and the freedom which we can enjoy in our business enterprise here in Mexico. Undoubtedly, a highly organized industrial nation will require a more complex system of legislation than a nation of less industrial development, but the grinding out of national and state legislation, passed and contemplated, should not come to a point where it becomes an oppression and an interference in rightful business, much intensified in times of already existing industrial depression.

The purpose of this letter is to enumerate the particular difficulties which we encountered in Los Angeles, which have forced us, in order to save our investments, to look for freedom in doing business for a place where we can recover our losses sustained through excessive legislation, and where we shall be able to do better than merely fill out numberless application blanks, pay taxes for permits, and obey the frequently arbitrary orders of frequently autocratic and ignorant inspectors.

C. Braubach

ByCo.
Chemisch-Pharmazeutische Fabrik, S. A.
Calle de Rosales 1
Mexico, D. F.
January 25, 1922

The Lime Fellowship of the Eastern Potash Corporation at New Jersey Agricultural Experimental Station

Occasionally in the solving of a research problem pertaining to the manufacture of chemicals, one must go to a field other than that embraced by the chemical laboratory or the semi-works plant. For example, in the manufacture of caustic potash and potassium nitrate from greensand, the Eastern Potash Corporation will obtain a large tonnage of a liming material containing approximately the same amount of CaO as is in ordinary limestone.

It was thought that this lime residue from potash extraction, which has been named limosil, would be applicable for the liming of soils. In order to test this possibility, research was transferred from the chemical laboratory to Nature's laboratory, and during the past year the New Jersey Agricultural Experiment Station at New Brunswick, under the direction of Dr. J. G. Lipman, has been investigating this problem in the greenhouses and also in the fields. The results to date indicate that this potash byproduct is as efficient as limestone or slaked lime in the liming of acid soils, the comparison of course being made on the basis of an equal CaO content.

As a great area of the soils, especially of the eastern United States, are in need of lime, this new by-product should not only cheapen the manufacture of domestic potash but also increase the yield from our farms. In carrying out such field and greenhouse experiments, the aim has been to parallel the actual practical tests on growing plants with laboratory studies of the effect of the lime on the various constituents of the soils, with the object of some day knowing just how the lime functions.

R. Norris Shreve

New York, N. Y.

Determination of Salt in Petroleum

Editor of the Journal of Industrial and Engineering Chemistry:

In the January number of THIS JOURNAL, **14** (1922), 80, Mr. George T. Dougherty calls attention to a method which was published under my name in an earlier number [**13** (1921), 325], for the determination of salt present in oil. He outlines a method used by the American Steel Foundries in Chicago for the same purpose, and, in going over it, I find we used about the same method when we first started our efforts toward determination of the amount of salt in oil.

It did not seem that we found all the salt present, however, owing to the difficulty of getting a proper extraction of the salt from the charred material left after burning the oil. Also, if the oil contained much salt water there was some loss due to spattering, which could not be prevented.

This led to the development of the method using acetone for extraction, which has the advantage of working on a larger quantity of oil; while it takes a little longer, it apparently extracts the salt water more thoroughly, as indicated by the following results, which are expressed in grams of salt per liter of oil:

DETERMINATION OF SALT IN CRUDE OIL SAMPLE

Method	Acetone	Burning
Test 1	0.70	0.51
Test 2	0.73	0.57

DETERMINATION OF SALT IN FUEL OIL SAMPLE

Method	Acetone	Burning
Test 1	0.95	0.81
Test 2	0.93	0.75

RALPH R. MATTHEWS

ROXANA PETROLEUM CORPORATION
WOOD RIVER, ILL.
March 24, 1922

Chilean Nitrate

Editor of the Journal of Industrial and Engineering Chemistry:

The savants and pseudo-savants who attended the meeting of the British Association at Bristol in 1898 were hoodwinked by Louis de Rougemont's story of fictitious adventure in northwestern Australia and startled by the Crookes' warning, equally absurd, as to the early exhaustion of the nitrate beds in Chile. The repetition of the Crookes' prophecy, omitting dates of course, will serve doubtless as an inspiration to authors of chemical treatises for many years to come; during the intervening time the public will still be told that our supply of iodine comes from seaweed.

Recently, however, another phase of the subject has developed, and technical journals and the daily press have been making direct reference to the nitrate deposits in the extreme north of Chile, thus complicating the Tacna-Arica controversy between Chile and Peru. On page 218 of your March issue you refer to the "potentially valuable nitrate beds" there; and, later, to the fact that "government experts" maintain that the district contains "valuable nitrate beds." Statements such as these smack so strongly of propaganda against Chile that they should be examined carefully before publication. The commercial nitrate deposits are far to the south. There is no more reason to assume that "valuable nitrate beds" occur in Tacna and Arica than that similar resources will be developed in every other arid region in the world.

A. W. ALLEN

BERKELEY, CAL.
March 15, 1922

In spite of a convincing demonstration last year that the by-product coking of bituminous coal could maintain itself better than could the beehive method in a period of industrial depression, and that by-product coking is continuing to supersede the older method, production of coke by-products during 1921 averaged in the neighborhood of one-third less than the 1920 output.

The Flow of Fluids through Commercial Pipe Lines—Correction

In the article under the above title [THIS JOURNAL, **14** (1922), 105] the following errors should be noted:

Page 112, 1st col., 3rd line in next to last paragraph, correct "Fig. 9" to read "Fig. 10."

Page 115, 2nd col., Section 4, the second equation should be

$$p = \frac{0.0538\, f\, l\, s\, Q^2}{D^5}.$$

Page 119, 1st col., 1st line, the sentence should read "From Fig. 17, $s = 0.00118$, etc." instead of "$z = 0.00118$, etc."

R. E. WILSON
W. H. MCADAMS
M. SELTZER

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
March 20, 1922

Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis

Editor of the Journal of Industrial and Engineering Chemistry:

The paper of the above title by Messrs. G. L. Kelly and E. W. Evers in the November issue of THIS JOURNAL treats a subject which is of supreme importance to the steel works chemist.

We feel it would interest other workers to know that independent investigators in Britain and America have established by their separate experience the practical advantages to be gained by the use of solid sodium hydroxide as an absorbent for carbon dioxide in the estimation of carbon.

It has been the standard practice since 1906 in the laboratories of Messrs. William Beardmore & Co., Ltd., Glasgow, to use solid sodium hydroxide as an absorbent in all carbon estimations. In this period a total approaching half a million estimations has been made and on this experience we can corroborate all the claims the authors put forward for the solid absorbent.

We have examined experimentally from time to time the proposals and claims made on behalf of apparatus and reagents both for liquid absorption and gaseous measurement and have found no sufficient reason to depart from our standard practice. This consists of the absorption of the carbon dioxide by the solid sodium hydroxide which is loosely packed in U-tubes with stoppers and side limbs.

The application of the use of soda asbestos noted in the authors' earlier paper [THIS JOURNAL, **8** (1916), 1038] was most opportune for us as it aided us in overcoming a war-time difficulty, and at the time the very real difficulty, of replacing impure and mechanically imperfect soda lye. Unfortunately we had the moisture difficulties noted by Messrs. Kelly and Evers. We have tried the absorption apparatus sketched therein and have found it admirably suited for the work.

JAS. MACWHIRTER, F.I.C.
Chief Chemist

LABORATORIES OF
MESSRS. WILLIAM BEARDMORE & CO. LTD.
ORDNANCE & STEEL WORKS
GLASGOW, SCOTLAND
January 26, 1922

Platinum Theft

On April 1 the laboratory of the Agricultural Experiment Station of the University of Florida lost by theft seven platinum evaporating dishes, average weight 18 to 21 grams, numbered as follows; 1, 2, 3, 11, 6, 7, 9.

R. M. RUPRECHT

WASHINGTON NOTES

DYE INVESTIGATION

The dye investigation is practically over, and as each witness has completed his testimony the fact is more forcibly and increasingly impressed upon us that the domestic dye industry will be completely vindicated. Seven weeks have been consumed in the hearings, and thus far not one person who has testified before the committee has shown that any monopolistic tendency exists. Importers, manufacturers, and users of dyes have all appeared and each, in turn, has testified that there is no monopoly of any kind. Even the small producer has failed to appear and testify to the existence of a monopoly.

The second point that the committee was charged to investigate was the question of lobbying. There has been no testimony that there has been lobbying, nobody has defined lobbying, and apparently there has been no attempt to prove that there has been lobbying. Senator Shortridge has repeatedly announced that if anyone had any evidence or wished to ask any questions relative to lobbying or monopoly they were free to appear and question the witnesses or the committee. Yet no one has appeared to propound such questions.

THE INEVITABLE

The friends of the American potash industry have always taken the attitude that all that was necessary was to give any unbiased judge the facts about this infant American industry and he could not do otherwise than decide that the enactment of a protective tariff was the only hope for the industry. In this they were not mistaken, as is evidenced by the provisions contained in the Tariff Bill, which has been passed by the House, approved by the Senate Finance Committee, and favorably reported to the Senate, and which briefly is as follows:

> That for a period of 5 years beginning on the day following the passage of the Tariff Act, there shall be levied, collected, and paid, on the actual potash (potassium oxide) content of potassium, chloride or muriate of potash, potassium, kainite, wood ashes and beet-root ashes, and all crude potash salts not specially provided for, a duty of 2.5 cents per pound for the first two years; 2 cents per pound for the third year; 1.5 cents per pound for the fourth year; and 1 cent per pound for the fifth year: thereafter the said potash content shall be free of duty.
>
> Potassium nitrate, or crude saltpeter, is admitted free of duty.

MUSCLE SHOALS

The House Committee on Military Affairs has completed its hearings and has printed eleven volumes containing the testimony that was given before the committee. On March 25, 1922, members of the Senate Committee on Agriculture and members of the House Committee on Military Affairs left Washington on an inspection trip of the Muscle Shoals project. About ten members from each branch of Congress made the trip, a number of members being detained in Washington because of other activities. The party was gone a little over five days and in that time made a complete inspection of everything in the vicinity that was in any way connected with the Muscle Shoals Project.

The members returned to Washington fully realizing that the Muscle Shoals undertaking is one of the most important that has ever been undertaken in this country for the development of our natural power. The consensus of opinion, however, seems to be that Congress cannot accept or reject any proposition relative to the purchase of this project but the importance of completing the Wilson Dam is thoroughly understood and indications are that an appropriation will be made available for the completion of the dam by the Government pending a decision relative to the various proposals which have been made for Muscle Shoals. Meantime the Senate Committee on Agriculture started its hearings on Monday, April 10.

METRIC SYSTEM

Hearings on the metric system bill have been completed. There is a strong sentiment even among some manufacturers of the country for the enactment of this bill into law, but this is offset by strong opposition on the part of certain manufacturers and interests that have organized to prevent the measure being adopted. Neither has the coöperation of the government departments been secured, some of the cabinet officers having declined to endorse the bill because they thought its enactment would cause confusion and expense to the Government. In the face of so much opposition it is very doubtful if any favorable action will be taken in the near future.

BOARD TO ADMINISTER MEDICAL FELLOWSHIPS

The National Research Council has appointed a special Board of eminent medical men to administer the National Fellowships in Medicine which the Research Council is able to offer through special gifts to it by the Rockefeller Foundation and General Education Board amounting to $100,000 a year for five years.

The members of the Board are: Victor C. Vaughan, *Chairman*, David L. Edsall, Joseph Erlanger, G. Carl Huber, E. O. Jordan, Dean D. Lewis, W. G. MacCallum, Lafayette Mendel, and W. W. Palmer.

The fellowships are open only to students who have already obtained the degree of M.D. or Ph.D. or have equivalent qualifications. Fellows will be appointed for one year with the privilege of applying for reappointment. Applications or requests for special information should be made to the Division of Medical Sciences, National Research Council, 1701 Massachusetts Ave., Washington, D. C.

KELP POTASH PLANT SOLD

The Kelp Potash Plant of the Bureau of Soils, U. S. Department of Agriculture, at Summerland, Cal., was sold and transferred on April 1 to Mr. Rodney Benson of Santa Barbara. The plant will be enlarged and put back into operation at once for the manufacture of "kelpchar" (a decolorizing carbon of very high activity), potash salts, and iodine.

LIME SPECIFICATIONS AND METHODS OF SAMPLING AND ANALYSIS

A meeting of Committee C-7 of the American Society for Testing Materials was held at the offices of the National Lime Association in Washington, D. C., on March 28 and 29. Specifications for sampling lime products, for determining the amount of available lime in quicklime and hydrated lime, together with specifications covering the use of lime in varnish manufacture, rag cooking, silica brick, sulfite pulp, and in the textile industry were presented to the whole committee for approval. These specifications will probably be presented to the Society at the annual convention for adoption as tentative standards. Considerable progress was reported by the subcommittees dealing with the use of lime in construction. The agricultural interests are working in conjunction with the American Association of Official Agricultural Chemists in an effort to develop standard methods of sampling and analysis.

New definitions of the terms quicklime and hydrated lime which are clear, concise, and complete, were adopted by the Committee, and careful study is being given to about one hundred other terms which are of special interest to this committee.

There will be a meeting of the Station Superintendents of the U. S. Bureau of Mines in Washington and Pittsburgh, the week of May 17. The meeting will be in Washington on Monday, Tuesday, and Wednesday, and in Pittsburgh on Thursday, Friday, and Saturday of that week. All of the Station Superintendents will be in attendance and the various problems with which they are confronted will be discussed at length.

Dr. R. B. Moore will leave on May 6 for a 2 months' trip abroad to carry out certain investigations for the Bureau of Mines.

The Bureau of Mines is arranging with a number of oil-producing companies in California to make motion picture films that will be useful in teaching the gospel of safety in the petroleum industry.

April 15, 1922

Personals

Dr. William A. Perlzweig, formerly research biochemist in the N. Y. branch of the Hygienic Laboratory, has accepted the position of chemist to the Medical Clinic in the Johns Hopkins University.

Dr. Lester A. Pratt, who has been in charge of the Research Laboratory of the Merrimac Chemical Co. for the past six years, has been made director of research for the same company.

Mr. E. M. Partridge, formerly chief chemist of the Refinite Co., Omaha, Neb., is now chemist for the Paige & Jones Chemical Co., Hammond, Ind

Mr. Henry G. Knight, formerly dean of agriculture of the Oklahoma Agricultural and Mechanical College and director of the Experiment Station, has been elected director and research chemist of the W. Va. Agricultural Experiment Station of the University of West Virginia. In November Mr. Knight was elected Honorary Fellow of Cornell University.

Mr. Frank E. Swindells left the employ of the Standard Chemical Co. on November 1, 1921, and joined the staff of the Bureau of Standards.

Mr. W. F. Washburn has resigned his position as assistant general manager of the Titan Co. A–S of Fredriksstad, Norway, and is now consulting engineer to the Titanium Pigment Co., Inc., Niagara Falls, N. Y.

Mr. John M. Grove, formerly connected with the Lee Tire & Rubber Co., of Conshohocken, Pa., and later with the N. J. Carspring & Rubber Co., Inc., of Jersey City, is now in charge of the laboratory of the New England Tire & Rubber Co., Holyoke, Mass.

Mr. Wm. C. McIntire has left the employ of the Cincinnati Chemical Works, Inc., and is now with the Sherwin-Williams Co., Chicago, Ill.

Mr. Wm. J. Burgess has resigned his position with the Electric Storage Battery Co., Philadelphia, to accept the position of chemical director of the Pennsylvania Coal Products Company's plant at Petrolia, Pa.

Mr. I. J. Jenks has accepted a position as professor of chemistry at the Northern Illinois State Teachers College, Dekalb, Ill. He previously occupied the position of chemist for the Brunswick Balke Collender Co., Muskegon, Mich.

Mr. Sam Tour, for a number of years metallurgist with the Technical Staff Office of the Chief of Ordnance, War Dept., Washington, D. C., is now with the Doehler Die Casting Co., Brooklyn, N. Y., in the same capacity.

Mr. Carl E. Hartwig, until recently associate chemist at Edgewood Arsenal, has accepted the position of research and development chemist with the Garfield Worsted Mills, at Garfield, N. J.

Mr. Walter S. Long has left the University of Kansas, where he was an assistant professor of chemistry, having in charge the work of the State Food Laboratory, to accept the position of City Chemist at Kansas City.

Mr. Chas. Braubach is technical director of the laboratories of the recently formed Chemisch-Pharmazeutische Fabrik ByCo. S. A., Calle de Rosales 1, Mexico D. F., of which company he is one of the founders.

Mr. H. G. Tanner has resigned his position as chief chemist of the U. S. Experimental Kelp-Potash Plant, Summerland, Cal., to assume the position of assistant professor in the department of chemistry, University of Oregon.

Mr. William C. Carnell died in Philadelphia on March 12, 1922, at the age of fifty-three. Mr. Carnell had been a member of the AMERICAN CHEMICAL SOCIETY since 1895, and had served on the Council and on various committees. He was very active in the Philadelphia Section, where his loss will be greatly felt. Mr. Carnell was a graduate of Lehigh University. Most of his professional career was spent in Philadelphia, in the field of acids and heavy chemicals. He became associated with Charles Lennig & Company in 1901, went to the Harrison Works, manufacturing heavy chemicals, pigments and paints, in 1913, returning to the Lennig Company in 1917. From May 1917 to August 1920 he was connected with the Rohm & Haas Co., after which time he again returned to Charles Lennig & Co.

Industrials

Mr. Robert C. Stanley, formerly First Vice President, was recently elected President of The International Nickel Company. Mr. Stanley has ordered a reorganization of personnel, involving as its chief feature a new department of Development and Research with headquarters at 67 Wall St., New York City.

The new department of the company is the outgrowth of a gradually maturing conviction that a study of its products and their successful use in the hands of the consumer is the key to the extension of tonnage distribution. Research departments at the mines, smelters, and refineries of the company, established during the last few years, have now been crystallized into a headquarters organization in intimate touch both with its own plant developments and with outside engineering developments, touching on the use of nickel and monel metal in all fields. This department will be under the direction of Mr. A. J. Wadhams, as Manager. Associated with him will be Dr. Paul D. Merica, Director of Research.

Mr. Wadhams has hitherto been manager of the large Bayonne refinery of this company and has for years been in direct charge of the manufacture of all of the company's products, and through this experience is fitted to an unusual degree for the new work which he is to undertake.

The Celite Products Company has recently established branch offices in Boston, Buffalo, Cincinnati, and Minneapolis, with the idea of securing increased business through direct concentrated effort.

The Combustion Engineering Corporation has recently opened a new branch office in Cleveland, Ohio, in charge of Mr. Frank Henderson.

The Freeport Sulphur Co., New York and Freeport, Texas, awarded contract on March 24 to Dwight P. Robinson & Co. for the design and construction of a complete sulfur mining plant at Hoskins Mound, Texas. The company now operates a large sulfur mining plant at Freeport, which contains one of the largest installations of oil-burning boilers in the world.

The Sarco Co., Inc., of New York has recently issued a bulletin—Sarco Temperature Control—illustrating various types of temperature regulators and their application.

The Century Wood Preserving Company has recently issued *Bulletin* **20,** "Storing and Seasoning Cross Ties," which gives an interesting discussion of the methods used by the company, factors influencing seasoning, possible deterioration during seasoning, and methods of handling and storing.

Twenty-five companies were organized during the month of March to engage in the manufacture and distribution of chemicals, drugs, and dyes. The aggregate indicated investment was $12,625,000, as compared with an aggregate of $5,200,000 in February. The average investment per company organized was $505,000 in March, and $236,363 in February. Three compaies were organized with an indicated investment of $1,000,000 or more during the month.

At the annual meeting of the Refractories Manufacturers' Association recently held in Chicago, the president urged the formation of a committee of thirteen to make a thorough industrial survey of operations in which refractories are utilized, to ascertain actual service conditions in the following fields: blast furnaces, not blast stoves; open hearth furnaces, soaking pits; heating, puddling and forging furnaces; all types of boilers; cement, lime and plaster kilns; window, plate, bottle and optical glass; annealing, malleableizing and air furnaces; water and coal-gas generators, gas producers; cupolas and gray iron furnaces; oil refineries; zinc, lead, and copper smelters; all types of by-product coke ovens; and all types of ceramic kilns.

Printed copies of patents may be obtained as follows: American, from the Commissioner of Patents, Washington, D. C., 10 cents each; Austrian, from Lehmann & Wentzel, Kaernthnerstrasse, 30, Vienna, 1, 20 cents each; British, from the Comptroller General, Patent Office, 25 Southampton Buildings, London, W. C. 2, 1 shilling each (plus 1d. postage); Canadian, manuscript copies only are available, estimates furnished in advance by Fetherstonhaugh & Smart, 50 Queen St., Ottawa; French, from l'Imprimerie Nationale, 87 Rue de Vielle de Temple, Paris, 1 franc each; German, from Reichspattentamt, Berlin, 5 marks each (lots of 20 or more, 2½ marks each).

BOOK REVIEWS

Benzine and Mineral Lubricants. By J. Formanek (translated from the German by Charles Salter). Cloth, $8^1/_2 \times 5^1/_2$. xii + 256 pp., 20 illustrations. Scott, Greenwood & Son, London; D. Van Nostrand Co., New York, 1921. Price, $5.00.

In this book, Formanek, who is a professor at the Bohemian Technical High School at Prague, considers the production, testing, and uses of gasoline, benzene, and petroleum lubricating oils. It embodies his experience as a motorist and a petroleum-products analyst, and it is intended for the guidance of users and testers of motor fuels.

There are 14 chapters, as follows:

Introductory
Petroleum: Its Composition and Treatment
Coal Tar Products
Brown-Coal, Shale and Peat-Tar Products
Products from Petroleum and Tar Residues
Testing Benzine and Benzene
Judging the Quality of Benzine and Benzene
Testing Mineral Lubricating Oils
Judging Mineral Lubricating Oils
Properties and Uses of Fuels
The Consumption and Efficiency of Various Fuels in Internal Combustion Engines
Suggested Improvements in Motor-Car Equipment
Safe Storage of Benzine and Benzene
First Aid in Cases of Gassing with Benzine

In discussing these various subjects, the author presents brief but informative descriptions of European and especially continental practice, but he has not accorded attention to American procedures. While the work will be of little value to the American petroleum chemist, the automotive engineer may wish to have it for reference, in order to have available the methods used in continental Europe for ascertaining the practical suitability of the materials currently employed for operating gasoline engines.

W. A. Hamor

Some Phases of Cost Accounting in the Chemical Industry. By C. B. E. Rosén, M. B. A., C. P. A. 18 pp. National Association of Cost Accountants, Bush Terminal Bldg., New York, 1921. Price, $0.75.

Mr. Rosén is evidently familiar with his subject and has brought his knowledge of accounting to bear on one of the most difficult problems in a field which has not been covered and in which no standard practice has been established.

More stress could be laid on Mr. Rosén's suggestion that a monthly determination of costs is apt to be misleading. If the costs for a three months' period are determined the conclusions reached are certain to be more accurate. This, of course, does not mean that detailed monthly costs should not be kept, but the conclusions drawn should be in the light of the three months' average.

The proper place for the deduction of by-products from the cost is a much mooted question, and the reviewer is rather inclined to differ with the author in this matter. Although it does not affect the costs whether deducted from raw materials or total manufacturing costs, it appears to the writer more logical that it should be deducted from the latter.

Mr. Rosén has laid stress on the item of repairs in chemical plants but he does not draw the line where repairs end and depreciation begins. It would seem that this is rather essential in setting up a reserve for both items so as not to confuse the repairs which are charged to conversion costs and depreciation which is charged to overhead. If the apparatus is to be kept in good condition by the repairs reserve, should there be so large an item set up as "10 to 20 per cent or more" for depreciation? Again, abnormally large discrepancies in "production reports" may eventually be charged off to profit and loss as suggested by the author but under no consideration should this be done until brought to the attention of the proper executive, for besides determining the costs one of the most essential reasons for the establishment of a cost accounting system is for the purpose of calling attention to just such discrepancies.

The items of cost are well considered but the detail of applying a cost accounting system to a chemical industry must be carefully studied; otherwise it will tend toward an elaborate and extensive collection of data which may be of little practical use when compiled.

Mr. Rosén's article is not a primer by any means, but presupposes a knowledge of cost accounting and might frighten the ordinary manufacturer. The latter should bear in mind that a knowledge of costs is the *sine qua non* of every successful business and that a vast majority of the failures of the country are brought about through the lack of knowledge of this essential requirement. Cost accounting is just as necessary to the chemical industry as to the shoe trade. A proper cost system is the guide to the conduct of a business and the details obtained in the collection of cost data are invaluable indications as to the trend of the business. They point out the cause of direct losses and draw attention to the efficiency or lack of efficiency in the various departments.

Mr. Rosén's pamphlet is a valuable contribution not only to the cost accountant but also to the chemical manufacturer.

William W. Caswell

Technical Records of Explosives Supply. 1915-1918. V—Manufacture of Sulfuric Acid by Contact Process. 128 pp., 43 figs. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1921. 19 × 28 cm. £1 5s. net.

Only the Mannheim and Grillo processes are treated of, 45 pages and 10 figures being devoted to the first, while 83 pages and 33 figures are assigned to the last-mentioned process. In the Mannheim plants iron pyrites was used as the source of sulfur. In the Grillo plants sulfur itself was burned to SO_2 on the ground that it required less skill to burn sulfur *per se* than to burn the sulfur out of pyrites and that, too, there was a saving in freight. The "lump" burners were of the usual type employed in England enclosed in sets of three with a flue in common and operated with dried air under slight pressure, but for "fines" Herreschoff burners were used. A small "lump" burner was erected beside each Herreschoff, the hot gas from which commingled in a common flue with the colder gas from the Herreschoff and brought the temperature of the mixture up to the optimum condition for oxide conversion. Careful precautions were used to prevent poisoning of the contact mass; yet when sulfur only, of high purity, was used it was found that the mass might suffer poisoning from arsenic picked up from the iron used in the construction of the plant. As in the previous works in this series[1] the apparatus and operations are described in minutest detail while quantities and yields are given. Of special interest is the preparation of the contact masses, both on the asbestos mat and the magnesium sulfate granule, as well as the recovery of the magnesium sulfate and platinum, together with the separation of platinum and iridium, from spent contact mass. No mention is made of the production of indurated refractory masses such as were produced in this country in the use of a magnesium sulfate foundation. This volume maintains the high standard of its predecessors in the series.

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[1] See This Journal, **13** (1921), 1176, **14** (1922), 250.

CHARLES E. MUNROE

Technical Records of Explosives Supply. 1915-1918. VI—Synthetic Phenol and Picric Acid. 97 pp., 50 figs. 19 × 28 cm. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1921. Price, 15s. net.

Some 38 pages with 26 figures are devoted to phenol, while 59 pages with 24 figures are assigned to picric acid, the figures including photographs, graphs, and folded plates. The topics, as presented, afford excellent examples of the versatility of chemistry, both as to the variety of the raw materials that may be used and the many different processes that may be followed. Thus four methods of producing phenol from benzene and three from cresols are given, as well as eight different methods for making phenolsulfonic acid. The records show careful study of operating conditions, though, as these manufactures were carried out chiefly by private firms, they were much less under direct control of the Department than those which have been dealt with in previous records of this series.[1] Hence American practice is drawn upon in this report and commended. Recalling that before the War the Ordnance Department, U. S. A., required picric acid to be made from synthetic phenol, we read here, "For the production of picric acid no material difference between coal-tar phenol and synthetic phenol has shown itself either in the laboratory or on the large scale" but some impurities, such as paraffin, appeared to act favorably, as a catalyst. An example of the difference in products following the attempt to convert laboratory experiments into large-scale operations is given on page 47 in the recovery of the nitrogen products of nitration. The average yield of picric acid for these factories was 70.6 per cent of the theory. The most efficient working results were 76.6 per cent. Embarrassment resulted from the fact that rejected picric acid could be sold to manufacturers of sulfur dyes at a higher price than the Government paid for that meeting its specifications. This publication seems not to have had the careful supervision which characterized the previous "Records." Instances of dropped letters and numbers and of misspelled words occur, while in cases such as "explosions," on page 56, "nitration process," on page 64, and "sifting," on page 64, one is left in doubt as to what the author sought to say. Nevertheless the book is a valuable one and will hold its place as an authority.

CHARLES E. MUNROE

Harze, Kunstharze, Firnisse, und Lacke. By HANS WOLFF, PH.D. 115 pp. Verein Wissenschaftlicher Verleger, Berlin, 1921. Price 25 cents.

This little volume represents a successful attempt at printing, in pocket size, the essential facts concerning resins, artificial resins, varnishes, and lacquers. At a time when many authors are trying to dilute the known facts into many paged volumes, concise publications such as this are quite welcome. In any case the specialist will still consult the source books, such as those by Tschirch, Dietrich, and Seeligmann.

Dr. Wolff discusses the occurrence of the balsams and resins in certain organs of plants; Tschirch's chemical classification of resins; chemical and physical methods of testing resins. In Chapter 2, the author discusses the composition, chemical tests for, and uses of: seven balsams; three resinotannol-resins (acaroid, benzoin, dragonsblood); three resene-resins (elemi, mastic, dammar); four resinol-acid resins; a resinol resin (guaiacum); the aliphato-resins; the gluco-resins; eight different gum resins; the lacto-resins; and the enzymo-resins. Five pages are devoted to the artificial resins—cumarone and "formolite" (phenol-formaldehyde condensation products).

Part II covers 33 pages devoted to varnishes and lacquers, driers, solvents, linseed-oil-varnishes, stand oil (or lithographic oil), oil lacquers, volatile lacquers, water lacquers, sealing wax, and the testing of varnishes and lacquers. Twelve pages are devoted to tables showing properties of the acids of the principal resins, the resinic acids of various turpentines, the ester resins, the gum resins, solubility, acid and saponification numbers of the balsams and resins, and the properties of twenty common solvents. The articles on cellulose acetate lacquers and cumarone resins will be of interest to many who are interested in protective coatings and waterproofing agents. The booklet is printed in clean-cut Roman type and is supplied with a good index. The work of the author as court expert for the Chamber of Commerce in Berlin is a guarantee of the authoritative character of the text. Chemists desiring a concise review of the resin and varnish industry will do well to procure the booklet for perusal.

FREDERIC DANNERTH

Patents and Chemical Research. By H. E. POTTS. 198 pp. University Press of Liverpool, 1921. Price, 8s. 6d.

This is an able presentation in condensed form of the elementary principles of English patent law in the language of the chemist-layman.

The author is an experienced English patent agent and he addresses himself primarily to the director of industrial chemical research and to the manager of the chemical manufacturing plant. The impelling purpose of the book is stated in the preface as follows:

> Therefore it is most desirable that chemists should familiarize themselves with the leading principles of patent law: first, to enable them to coöperate with the patent agent and thus contribute to the object of obtaining secure protection for their inventions, and, second, so that their criticism will stimulate patent agents to maintain the highest level of professional skill. In this way, better work will be done, and the greatest benefits will be derived from the patent system.

Throughout the text, hypothetical as well as actual chemical cases are freely used with remarkable success for purposes of illustration. The first chapter is entitled "Patents as an Element of Business Policy," and deals especially with the relative advantages of patenting as against secret working as a means of protecting valuable chemical processes under the English law. The remaining chapters, except the last, deal with the cardinal principles of the English patent system. The last chapter treats briefly of the patent systems of other countries.

The book is well indexed but one might wish for more clearly marked subdivisions of the subject matter of the different chapters. There is a special index of cases, and subject titles of many of these cases are given in chemical terms—a distinct help to the chemist-reader.

The exposition primarily concerns the English patent system rather than that of the United States, and although many fundamental concepts are common to both systems it may not be amiss to caution the American chemist-reader against applying too directly in this country conclusions derived from a study of this book alone. The chapter entitled "Patents in Other Countries" will be helpful in indicating the numerous possible pitfalls in this direction.

In the opinion of the reviewer no single publication in recent years has greater potentialities for increasing the real effectiveness of systematic industrial research than the appearance of this book. A corresponding book dealing primarily with the United States patent system is greatly to be desired.

A. S. MCDANIEL

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[1] THIS JOURNAL, **13** (1921), 1176; **14** (1922), 250.

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

March

Chile still awaits a betterment in the **nitrate trade** of Europe and the United States. The prices on nitrate which were fixed on October 27, 1921, terminate on June 30, 1922, and lower prices are anticipated thereafter. (P. 546)

The year 1921 was marked by an exceedingly acute depression in the **iron ore** mining industry of Vizcaya, Spain, the chief source of wealth of that district. (Pp. 569–70)

In order to direct intelligently the work of searching for **petroleum** in Australia and New Guinea, the State Minister of Mines for New South Wales has announced that the State Government of that territory will assist the prospectors by advice and by subsidizing operations conducted at approved sites. (P. 573)

The quantity of **shale oil** produced in Australia during the year ending June 30, 1920, was 1,539,438 gal., and for the succeeding fiscal year, 2,612,976 gal. Shale deposits are found in numerous places in New South Wales, and it is asserted by the minister of mines for that territory that these deposits are the richest in the world. It is further stated that there is enough petrol in two of the sections alone to keep Australia for years absolutely independent of the outside world market if the present methods of extracting oil from the shale prove successful. (P. 573)

The **oil industry** in Poland has recently undergone a beneficial change because government restrictions have been very largely abandoned in favor of free trade, both for domestic and export business. The Bureau of Foreign and Domestic Commerce has on file statistics showing domestic and foreign deliveries of Polish oil in 1920. (P. 573)

The **petroleum** fields of Mendoza-Neuquen are described. (Pp. 573–4)

The Bureau of Foreign and Domestic Commerce has on file a report from Consul Henry D. Baker relative to the occurrence of oil in Trinidad. (P. 574)

Beginning with January 1, 1922, the use of the **metric system** of weights and measures is required in Lithuanian commercial and industrial establishments. (P. 590)

An account of the working of the **phosphate** deposits of Nauru and Ocean Islands has just been published in a report by the British senior trade commissioner of Australia. (P. 594)

A possible market for **chemical fertilizers** is reported in Indo-China. (P. 594)

Details in regard to the effect on the Scotch textile industries of the British **embargo** now placed on foreign **dyestuffs** may be had upon application to the Textile Division of the Bureau of Foreign and Domestic Commerce. (P. 616)

During the first months of 1921 about half of the automobiles in Pernambuco were using **alcohol fuel**, but to-day 90 per cent of these vehicles have resumed the use of gasoline. The reasons for this decline in the use of alcohol fuel are given and it is claimed that in spite of this abandonment of alcohol as a motor fuel everyone in Pernambuco still believes that alcohol is the future automobile fuel and, furthermore, considers it a patriotic duty as well as an economy to use alcohol. (Pp. 621–2)

The United States **petroleum** export trade in 1921 is reviewed. The report includes charts giving graphic presentation of exports by months for the years 1920 and 1921, as well as tables giving statistics of exports for the same period. (Pp. 638–40)

A record shallow well has been drilled in the Tampico oil fields, the daily production of which is estimated at 60,000 bbls. (P 640)

The exploration of Bolivian **oil** fields by Swedish and German geologists is announced, but it is probable that the extraction will not begin for several years owing to the difficult nature of the country. (P. 640)

The period for the sale of **saccharin** as a substitute for sugar in Italy has been extended to June 30, 1922. Saccharin imported under this provision is admitted free of duty. (P. 650)

The operation of the **copper** mines in Mexico will soon be resumed. (P. 654)

A mining company in China is prepared to supply metallurgical **manganese** to the extent of 40,000 tons per annum and chemical manganese in small tonnage, the composition of the various grades being guaranteed. Further information may be secured from the Far Eastern Division, Bureau of Foreign and Domestic Commerce. (P. 656)

The production of Alsatian **potash** during 1921 shows a considerable decrease as compared to 1920. (P. 660)

Statistics are given showing the production of **crude oil** in Rumania during 1920 and 1921. (Pp. 700–1)

Petroleum possibilities in the Cadiz, Spain, Consular District are announced. The officials are very hopeful of important developments, provided foreign companies can be sufficiently interested to explore the fields thoroughly. (P. 701)

The revised **Spanish tariff**, which went into effect February 16, 1922, contains important changes in duties on the following American products: scientific apparatus; chemicals, including aniline oils, caustic soda and caustic potash, slag, superphosphate of lime; dyes and dyestuffs, coal tar; and petroleum products. (Pp. 712–3)

Certain **Italian export** restrictions have been removed on ingots of gold and silver containing platinum, mineral oils including petroleum, benzine, and charcoal. (P. 714)

Preparations are under way for the exploitation on a large scale of the **potash** deposits near Suria, Spain. It is believed that agriculture will be given a great impetus by the development of these potash deposits. (P. 723)

The value of **mineral production** in Canada in 1921 was $170,000,000 as compared with $227,859,665 in 1920. (P. 724)

Bleached pulp for the manufacture of newsprint which is being made in New South Wales has been officially inspected and approved. The pulp is made from the mountain gum tree, of which immense tracts are available. (P. 762)

Regulations relative to carrying out provisions of the Ecuadorean law relative to **petroleum** concessions may be consulted in the Bureau of Foreign and Domestic Commerce. (P. 762)

The Fuel Division of the Bureau of Foreign and Domestic Commerce has on file a statement that an electrochemical process has been perfected for the manufacture of metallic **calcium** and of 97.5 per cent **caustic soda**, free from chloride of soda. It is claimed for the process that it is much cheaper than others now in use. (P. 763)

Important changes in **import duties** affecting the following American products are imposed by the revised New Zealand tariff: calcium carbide; cottonseed oil; linseed (bulk); benzene; gasoline; kerosene; crude petroleum; paints, and colors. (Pp. 778–81)

Statistics are given relative to the **gum arabic** trade of the Sudan. (P. 786)

SPECIAL SUPPLEMENTS ISSUED

Brazil
British West Indies
Portugal
Spain
United Kingdom
Bradford
Trade of French West Africa for 1920
Senegal
Dahomey
French Guinea
Trade of Straits Settlements for 1920
Trade of Turkey for 1920
Trinidad and Tobago

STATISTICS OF EXPORTS TO THE UNITED STATES

Brazil and Peru—(P. 571)
Rubber
Ceylon—(P. 594)
Rubber
Tunis—(P. 591)
Marjoram
Olive oil
Argentine—(P. 652)
Linseed
Cairo—(P 786)
Gum arabic
Oil, crude, fusel

CURRENT PUBLICATIONS

NEW BOOKS

Clinical Diagnosis: A Textbook of Clinical Chemistry for Medical Students, Laboratory Workers, and Practitioners of Medicine. Charles Phillips Emerson. 5th edition, rewritten. 726 pp. Price, $7 50. J. B. Lippincott Co., Philadelphia.

Coal: Its Properties, Analysis, Classification, Geology, Extraction, Uses and Distribution. Elwood S. Moore. 462 pp. 142 figures. Price, $5 00. John Wiley & Sons, Inc., New York.

Colloid Chemistry of the Proteins. Part I. Wolfgang Pauli. Translated by P. C. L. Thorne. 140 pp. Price, 8s. 6d. J. & A. Churchill, London.

Combustion: The Chemistry of Combustion. J. Newton Friend. 110 pp. Price, 4s. net. Gurney & Jackson, London.

Dictionary: Dictionnaire Anglais-Français-Allemand de Mots et Locutions Intéressant la Physique et la Chimie. T. Cornubert. 300 pp. Price, 47fr. Dunod, Paris.

Electrodynamics: An Introduction to Electrodynamics from the Standpoint of the Electron Theory. Leigh Page. 134 pp. Illustrated. Price, $2.00. Ginn & Co., Boston.

Engineering Drawing: An Introduction to Engineering Drawing. J. Duncan. 158 pp. Illustrated. Price, $1.40. The Macmillan Co. New York

Explosives: Technical Records of Explosives Supply, 1915–1918. No. 5. Manufacture of Sulfuric Acid by Contact Process. 128 pp. Illustrated. Price, 26s. **No. 8. Solvent Recovery.** 22 pp. Price, 3s. 3d. Ministry of Munitions and Department of Scientific and Industrial Research. H. M. Stationery Office, London

Fire Assaying: A Textbook of Fire Assaying. Edward E. Bugbee. 254 pp. 51 figures. Price, $3.00 net. John Wiley & Sons, Inc., New York.

Fuel and Lubricating Oils for Diesel Engines. W. Schenker 126 pp. Price, $3.00. D. Van Nostrand Co., New York.

Fuel and Refractory Materials. A. H. Sexton and W B. Davidson. New edition, revised and enlarged. Illustrated. 382 pp. Price, $4 00. D. Van Nostrand Co , New York.

Gas: The Distribution of Gas. Walter Hole. 4th edition, rewritten and enlarged. 699 pp. Illustrated. Price. 50s. net Benn Bros., Ltd., London.

Gas: Messung Grosser Gasmengen. L. Litinsky. Chemical Technology Series, edited by A. Binz 274 pp. Price, paper, 525 M, bound, 585 M. Otto Spamer, Leipzig.

Gas Chemists' Handbook. Compiled by Chemical Committee, Technical Section of American Gas Association. 2nd edition. 608 pp Price, $6.00. American Gas Association, New York.

Geologie et Mineralogie Appliquées à l'Art de l'Ingenieur. L. de Launay. 418 pp. Price, 50 fr. J.-B. Bailliere et Fils, Paris.

Heat Conduction: Introduction to the Mathematical Theory of the Conduction of Heat in Solids. H. S. Carslaw. 2nd edition, revised. 268 pp. Illustrated. Price, $9.00. The Macmillan Co., New York.

Heating and Ventilation. John R. Allen and J H. Walker. 2nd edition. 330 pp. Illustrated. Price, $3.50. McGraw-Hill Book Co., Inc., New York.

History of Chemistry: A Concise History of Chemistry. T. P. Hilditch. 2nd edition, revised. 276 pp. Price, 6s. Methuen & Co., Ltd., London.

Industry and Human Welfare. William L. Chenery. Price, $1.75. The Macmillan Co., New York.

Isotopes. F. W. Aston. 152 pp. Price, 9s. Edward Arnold & Co., London.

Liquid Fuel: Burning Liquid Fuel; A Practical Treatise on the Perfect Combustion of Oils and Tars, Giving Analysis, Calorific Values and Heating Temperatures of Various Gravities; with Information on the Design and Proper Installation of Equipment for All Classes of Service. William Newton Best. Revised and enlarged edition. 341 pp. Price, $5.00. U. P. C. Book Co., New York.

Medical Research Report: Report of the Medical Research Council for the Year 1920–21. 114 pp. Price, 3s. 6d. net. H. M. Stationery Office, London.

Metallography: An Introduction to the Study of Metallography and Macrography. Léon Guillet and A. Portevin. Translated by L. Taverner. 289 pp. Price, 30s. G. Bell & Sons, Ltd., London.

Oil Encyclopedia. Marcel Mitzakis. 551 pp. Price, 21s. Chapman & Hall, Ltd., London.

Oils: Chemical Technology and Analysis of Oils, Fats and Waxes. Julius Isidor Lewkowitsch. Edited by George H. Warburton. 6th edition, rewritten and enlarged. Price, $12.00. The Macmillan Co., New York.

Papier. G. Dalén. **Einzelschriften zur Chemischen Technologie.** Edited by Th. Weyl. Vol. I Pt. 1. 2nd edition. 122 pp. Price, 25 M. J B. Barth, Leipzig.

Petroleum. A Treatise on the Geographical Distribution and Geological Occurrence of Petroleum and Natural Gas; the Physical and Chemical Properties, Production, and Refining of Petroleum and Ozokerite; the Characters and Uses, Testing, Transport and Storage of Petroleum Products, and the Legislative Enactments Relating Thereto, Together with a Description of the Shale-Oil and Allied Industries. Sir B. Redwood. 4th edition, revised and rewritten. 3 vols. 1383 pp. Illustrated. Price, set, $39.00. D. Van Nostrand Co., New York.

Physico-Chemical Problems Relating to the Soil. Report of General Discussion Held by the Faraday Society. 368 pp. Price, 10s. 6d net. The Faraday Society, London.

Potash. Sydney J. Johnstone. New edition, revised and enlarged. 122 pp. Price, 6s net John Murray, London.

Practical Physiological Chemistry: A Book Designed for Use in Courses in Practical Physiological Chemistry in Schools of Medicine and of Science. Philip Bovier Hawk. 7th edition, revised. 675 pp. Illustrated. Price, $5.00. P. Blakiston's Son & Co., Philadelphia.

Qualitative Analysis: An Outline of Qualitative Analysis of Inorganic Substances. Horace G. Byers. 227 pp. Price, $2.00. D. Van Nostrand Co., New York.

Rubber. Edith A. Brown. 88 pp. Illustrated. 2nd edition. Price, $1.50. The Macmillan Co., New York

Soap-Making Manual. A Practical Handbook on the Raw Materials, Their Manipulation, Analysis and Control in the Modern Soap Plant. E. G. Thomssen. 251 pp. Illustrated. Price, $4.00. D. Van Nostrand Co., New York.

Turbines à Vapeur. M. Poincet. 336 pp. Illustrated. Price, 35 fr. J.-B. Baillière et Fils, Paris.

Universities and Scientific Life in the United States. Maurice Caullery. 286 pp. Price, $2 50. Harvard University Press, Cambridge.

Zirconium and Its Compounds. Francis P. Venable. **A. C. S. Monograph Series.** 173 pp. Price, $2.50. Chemical Catalog Co., Inc., New York

RECENT JOURNAL ARTICLES

Ammonia: The Oxidation of Ammonia. C. S. Imison and W. Russell. *Journal of the Society of Chemical Industry*, Vol. **41** (1922), No. 4, pp. 37*t*–45*t*.

Atoms and Isotopes. Ellwood Hendrick. *Chemical and Metallurgical Engineering*, Vol. **26** (1922), No. 13, pp. 583–87.

Cellulose: Problems of Cellulose Chemistry. Emil Heuser. *Paper*, Vol. **29** (1922), No. 23, pp. 7–10.

Clay: Suggested New Methods in the Preparation of Dust-Pressed Bodies. H. Spurrier. *Journal of the American Ceramic Society*, Vol. **5** (1922), No. 3, pp. 151–56

Coal: Bituminous Coal as Generator Fuel. W. A. Dunkley. *American Gas Journal*, Vol. **116** (1922), No. 11 (whole No. 3341), pp. 249–52, 260–61.

Coal: Neue Beiträge zur Enstehung und Chemischen Struktur der Kohle. Franz Fischer and Hans Schrader. *Brennstoff-Chemie*, Vol. **3** (1922), No 5, pp. 65–72

Flue-Gases: Practical Interpretation of Automatically Recorded Volumetric Percentages of CO_2 in Flue-Gases. W E. Appleby. *Chemical Engineering and Mining Review*, Vol. **14** (1922), No. 161, pp. 156–60.

Fluorspar in Open-Hearth Practice. S. Schleicher. *The Iron Age*, Vol. **109** (1922), No. 11, pp. 783–84. Translated from *Stahl und Eisen*.

Fuel: Causes and Prevention of Power and Fuel Wastes. H. D. Martin. *Color Trade Journal*, Vol. **10** (1922), No. 3, pp. 98–103.

Glass: Some Aspects of Science Applied to the Glass Industry. C. H. Kerr. *The Glass Industry*, Vol. **3** (1922), No. 4, pp. 69–71

Glass: An Autoclave Test for the Grading of Chemical Glassware. W. L. Baillie and F. E. Wilson. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No 4, pp. 45*t*–55*t*.

Iron and Steel Classified for Designers. William J. Merten. *Forging and Heat Treating*, Vol. **8** (1922), No. 3, pp. 155–60.

Iron: Researches on the Electrodeposition of Iron. W. E. Hughes. *Brass World*, Vol. **18** (1922), No. 3, pp. 80–85.

Metallurgy: The Correlation of Metallurgical Statistics. H. A White *Journal of the Chemical, Metallurgical and Mining Society of South Africa*, Vol. **22** (1921), No. 6, pp. 97–106.

Monel Metal, A Natural Nonferrous Alloy. Morris A. Hall. *Brass World*, Vol. **18** (1922), No. 3, pp. 76–79.

Open-Hearth Furnaces: Design of Open-Hearth Furnaces. A. D. Williams. *The Iron Age*, Vol. **109** (1922), No. 9, p. 577; No. 11, p. 717; No. 13, pp. 853–55.

Sewage: Further Experiments with Activated Sludge. E. Hannaford Richards and G. C. Sawyer. *Journal of the Society of Chemical Industry*, Vol. **41** (1922), No. 5, pp. 62*t*–72*t*.

Steel: Influenza della Temperatura sulle Proprietà Meccaniche della Ghisa. F. Graziana. *Giornale di Chimica Industriale ed Applicata*, Vol. **4** (1922), No. 2, pp. 53–56.

Tanning: A Critical Study of the Determination of the Active Constituents of Synthetic Tanning Materials by the Hide Powder Method. S. Kohn, J. Breedis and E. Crede. *Journal of the American Leather Chemists Association*, Vol. **17** (1922), No. 4, pp. 166–80.

Tin: The Metallurgy of Tin. Walter H. Jacobson. *The Metal Industry*, Vol. **20** (1922), No. 3, pp. 103–5.

Water Resistant Glues: Casein and Blood Albumin. Robert Herman Bogue. *Chemical Age*, Vol. **30** (1922), No. 3, pp. 103–6.

Wood: Proper Use of Wood in Connection with Dyehouses and Bleacheries. Joseph Woodman. *Textile Colorist*, Vol. **44** (1922), No. 520, pp. 245–47.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Accidents at Metallurgical Works in the United States during the Calendar Year 1920. W. W. Adams. *Technical Paper* **297.** 28 pp. Paper, 5 cents.

Analysis of Detonating and Priming Mixtures. C. A. Taylor and W. H. Rinkenbach. *Technical Paper* **282.** 33 pp. Paper, 5 cents.

Analytical Distillations of Typical Shale Oils. M. J. Gavin. *Reports of Investigations* **2332.** 12 pp. Issued March 1922.

Bibliography of Literature on Sampling. Compiled by W. J. Sharwood and M. W. von Bernewitz. *Reports of Investigations* **2336.** 1 p. Issued March 1922.

Drilling and Dustiness of Metal-Mine Air. D. Harrington. *Reports of Investigations* **2339.** 6 pp. Issued March 1922.

Epsomite. R. B. Ladoo. *Reports of Investigations* **2333.** 5 pp. Issued March 1922.

Fighting a Mine Fire with Its Own Gases. C. A. Allen and A. C. Watts. *Reports of Investigations* **2325.** 8 pp. Issued February 1922.

Metal-Mine Accidents in the United States during the Calendar Year 1920. W. W. Adams. *Technical Paper* **299.** 99 pp. Paper, 10 cents. 1922.

Performance of Fan-Pipe Installations in Metal Mines. D. Harrington. *Reports of Investigations* **2320.** 4 pp. Issued February 1922.

Physiological Effects of Exposure to Low Concentrations of Carbon Monoxide. R. R. Sayers, F. V. Meriwether and W. P. Yant. *Reports of Investigations* **2338.** 6 pp. Issued March 1922.

Procedure for Establishing a List of Permissible Carbon Monoxide Indicators. Fees, Character of Tests, and Conditions under Which Indicators Will Be Tested. *Schedule* **18.** 7 pp.

Production of Gasoline by Cracking Heavier Oils. E. W. Dean and W. A. Jacobs. *Technical Paper* **258.** Paper, 5 cents.

Quarry Accidents in the United States during the Calendar Year 1920. *Technical Paper* **295.** 66 pp. Paper 10 cents. 1922.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. *Reports of Investigations* **2330.** 53 pp. Issued February 1922.

Specifications for Petroleum Products Adopted by the Interdepartmental Petroleum Specifications Committee, Effective January 23, 1922. Amended March 1, 1922. These specifications have been officially adopted by the Federal Specifications Board for the use of the various departments and independent establishments of the Government. *Technical Paper* **305.** 40 pp. Paper, 5 cents.

Summarized Reports of Principal Investigations Being Conducted by the Bureau of Mines for Fiscal Year beginning July 1, 1921. 186 pp.

Test of Hand Extinguishers on Zinc-Dust Fires. S. H. Katz and J. J. Bloomfield. *Reports of Investigations* **2335.** 6 pp. Issued March 1922.

The Northwest Experiment Station of the Federal Bureau of Mines. C. E. Williams. *Reports of Investigations* **2337.** 4 pp. Issued March 1922.

The Smoke Problem. O P. Hood. *Reports of Investigations* **2323.** 5 pp. Issued February 1922.

The Use of Electrolytes in the Purification and Preparation of Clays. H. G. Schurecht. *Technical Paper* **281.** 47 pp. Paper, 10 cents.

Use of Low-Pressure Gas Burners in Oil-Feed Boilers. M. P. Youker. *Reports of Investigations* **2329.** 8 pp. Issued February 1922.

Bureau of Standards

Weighing by Substitution. C. A. Briggs and E. D. Gordon. *Technologic Paper* **208.** Paper, 5 cents.

Congress

Tariff: An Act to Provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States, and for other purposes. H. R 7456. Report 595. Reported by Mr. McCumber with amendments April 10, 1922 (Calendar Day, April 11). **438 pp.**

Congressional Committees

Decimal System. American decimal system of weights and measures, by Samuel Russell. Statement, December 20, 1921. 20 pp 1922.

Hearings before the Committee on Finance, United States Senate, on the Proposed Tariff Act of 1921 (H. R. 7456). Free List. Revised and Indexed. 693 pp.

Metric System. Ladd Metric Bill, Its Fallacy and Futility. Statement of Samuel Russell, December 16, 1921. 8 pp. 1922.

Metric System. Statement by Samuel S. Dale at hearings before subcommittee on S. 2267, to fix metric system of weights and measures for certain uses, December 14, 1921. 24 pp. 1922.

Muscle Shoals Propositions. Hearings before the Committee on Military Affairs, House of Representatives

Part 11—Statements of F. D. Mahoney (Alabama Power Co.), Hon. S. Hubert Dent, Jr., Thomas W. Martin (President, Alabama Power Co.), Hon. William B. Oliver, M. C., Alabama, Major John G. Booton, Ordnance Department, U. S. A. February 27–March 2, 1922. 195 pp.

Part 12—Statements of Frederick E. Engstrum, Hon. Marion Butler, Thomas W. Martin, Francis E. Frothingham J. H. Levering. William B. Mayo, Gray Silver, Hon. William B. Oliver, Hon. Ed. B. Almon, Hon. William B. Bankhead, Hon. Joseph W. Byrns, Hon John McDuffie, Col. J. W. Joyes and Dr. Charles L. Parsons. March 3, 6, 7, 8 10, and 13, 1922. 240 pp.

Department of Commerce

Artificial Dyestuffs Imported into the United States 1913–14. Supplemental Statistics to Accompany Agents Series 121. 47 pp.

General Supply Committee

Specifications and Proposals for Supplies, Fiscal Year 1923. Class 4. Drugs and Medicines, and Chemicals. 34 pp.

Geological Survey

Cement in 1920. E. F. Burchard. Separate from Mineral Resources of the United States, 1920, Part II. 20 pp. Published March 7, 1922.

Field Examination of Water. W. D. Collins. 13 pp.

Quicksilver in 1920. F. L. Ransome. With a Supplementary Bibliography. I. P. Evans. Separate from Mineral Resources of the United States, 1920, Part I. 21 pp. Published March 27, 1922.

Stone in 1920. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1920, Part II. 38 pp. Published March 6, 1922.

Labor Statistics Bureau

Carbon Monoxide Poisoning. Alice Hamilton *Bulletin* **291.** Industrial Accidents and Hygiene Series. 47 pp. Paper, 10 cents.

Public Health Service

City Health Officers, 1921, Directory of Those in Cities of 10,000 or More Population. *Reprint* **702** from Public Health Reports. 12 pp. Paper, 5 cents.

Improved Method for the Preparation of Vitamin-Activated Fuller's Earth. Atherton Seidell. *Public Health Reports* **37** (April 7, 1922), 801–3.

Keeping Qualities of Market Samples of Neoarsphenamine While in Ampule. G. B. Roth. *Reprint* **700** from Public Health Reports. 19 pp. Paper, 5 cents.

State and Insular Health Authorities, 1921: Directory, with Data as to Appropriations and Publications. *Reprint* **706** from Public Health Reports. 20 pp. Paper, 5 cents.

The Loading of Filter Plants. H. W. Streeter. *Public Health Reports* **37** (March 31, 1922), 741–53.

United States Public Health Service, Information for Persons Desiring to Enter Regular Corps of Service. R. C. Williams. *Reprint* 719 from Public Health Reports. 6 pp.

Tariff Commission

Tariff Information Surveys. Revised edition, 1922. FL-24. On articles in Paragraphs 536–544 of Tariff Act of 1913 and related articles in other paragraphs Cryolite, graphite, and magnesite. 65 pp Paper, 5 cents.

MARKET REPORT—APRIL, 1922

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

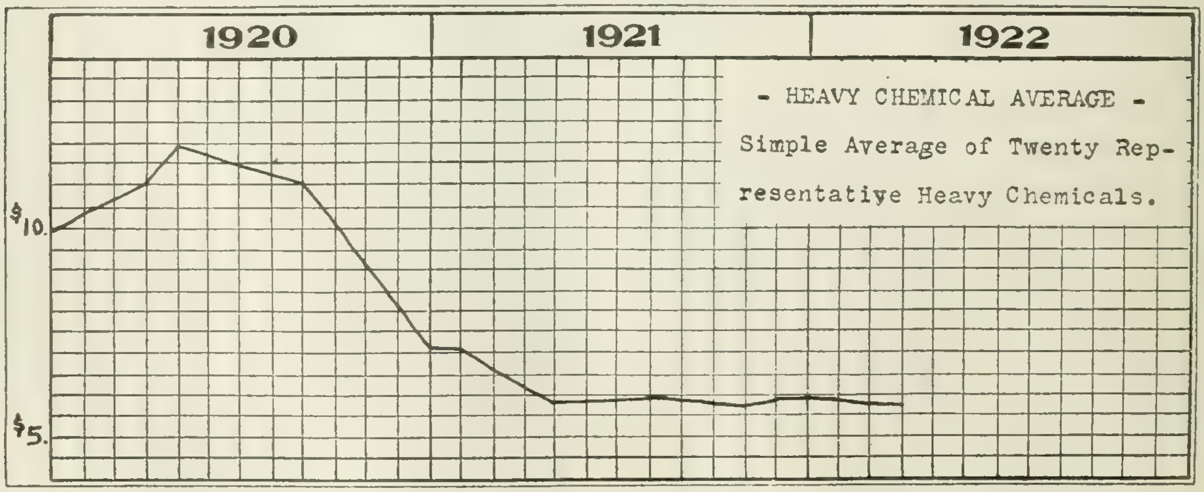
INORGANIC CHEMICALS

		Apr. 1	Apr. 15
Acid, Boric, cryst., bbls	lb.	.12¾	.12¾
Hydrochloric, com'l, 20°	lb.	.01¼	.01¼
Hydrofluoric, 30 p. c., bbls	lb.	.07	.07
Hydriodic, sp. gr. 1.150	oz.	.19	.19
Nitric, 42°	lb.	.06¾	.06¾
Phosphoric, 50% tech	lb.	.09	.09
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66° tks. wks.	ton	16.00	16.00
Oleum 20%	ton	22.00	22.00
Alum, Ammonia, lump	lb.	.03½	.03½
Potash, lump	lb.	*.03¼	*.03¼
Chrome	lb.	.06½	.06½
Soda, ground	lb.	.03½	.03½
Aluminium Sulfate (iron-free)	lb.	.02½	.02½
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	.07½	.07½
Ammonia, Anhydrous	lb.	.30	.30
Ammonia Water, drums, 26°	lb.	.07½	.07½
Arsenic, white	lb.	.07	.06¾
Barium Chloride	ton	*80.00	*100.00
Nitrate	lb.	*.06	*.06
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works,	100 lbs.	1.75	1.75
Borax, cryst., bbls	lb.	.05½	.05½
Bromine, pure, wks	lb.	.23	.23
Calcium Chloride, fused, f. o. b. N. Y.	ton	24.50	24.50
Chalk, precipitated, light	lb.	.04	.04
China Clay, imported	ton	18.00	18.00
Chlorine, liquid	lb.	.06	.06
Copper Sulfate	100 lbs.	5.40	5.40
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.05	4.05
Lead Acetate, white crystals	lb.	.11	.11
Nitrate	lb.	.15	.15
Red American	lb.	.08	.08
White American	lb.	.07¼	.07¼
Lime Acetate	100 lbs.	1.75	1.75
Lithium Carbonate	lb.	1.40	1.40
Magnesium Carbonate, tech	lb.	.06	.06
Magnesite	ton	72.00	50.00
Mercury flask	75 lbs.	49.00	50.00
Phosphorus, yellow	lb.	*.25	*.25
Red	lb.	*.25	*.25
Plaster of Paris	bbl.	4.25	4.25
Potassium Bichromate	lb.	.10	.10
Bromide, imported	lb.	*.17	*.16
Carbonate, calc., 80–85%	lb.	.04½	.04½
Chlorate, cryst	lb.	*.06	*.06
Hydroxide, 88–92%	lb.	*.06	*.06
Iodide, bulk	lb.	3.15	3.15
Potassium (*Concluded*)			
Nitrate	lb.	.08	.08
Permanganate U. S. P.	lb.	*.14	*.14
Prussiate, Red	lb.	*.65	*.65
Yellow	lb.	.26½	.27½
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.43¾	.44
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	*1.80	*1.80
Caustic, 76%	100 lbs.	*3.60	*3.60
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.00	2.00
Bichromate	lb.	.07½	.07¼
Bisulfite, powd	lb.	.04¼	.04½
Chlorate	lb.	.07	.07
Cyanide, 96–98%	lb.	.26	.25
Fluoride, technical	lb.	.10	.10
Hyposulfite, bbls	100 lbs.	3.25	3.25
Nitrate, 95%	100 lbs.	2.85	2 85
Nitrite	lb.	.09½	.09½
Prussiate, yellow	lb.	.16¾	.16
Phosphate (di-sodium), tech.	lb.	.04	.04
Silicate, 40°	lb.	.01	.01
Sulfide, 60% fused	lb.	*.04¼	*.04¼
Strontium Nitrate	lb.	*.07½	*.07½
Sulfur, flowers	100 lbs.	3.00	3.00
Crude, mines	long ton	14.00	14.00
Talc, American, white	ton	17.00	17.00
Tin Bichloride, 50% sol'n	lb.	.10¼	.10¼
Oxide	lb.	.37	.37
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.08	.08

*Resale or Imported (not an American makers' price).

ORGANIC CHEMICALS

		Apr. 1	Apr. 15
Acetanilide, U. S. P. bbls	lb.	.31	.31
Acid, Acetic, 28 p. c.	100 lbs.	2.37½	2.37½
Glacial	lb.	.08½	.08½
Acetylsalicylic, 100 lbs.	lb.	.80	.80
Benzoic, U. S. P., ex-toluene	lb.	.58	.55
Carbolic, cryst., U. S. P., drs.	lb.	.14	.14
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, kegs	lb.	*.45	*.45½
Oxalic, cryst., bbls., wks.	lb.	.11½	.11½
Pyrogallic, resublimed	lb.	1.60	1.60
Salicylic, bulk, U. S. P.	lb.	.26	.26
Tannic, U. S. P., bbls	lb.	.65	.65
Tartaric, crystals, U. S. P.	lb.	*.26	*.26½
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.09	.09
Alcohol, denatured, complete	gal.	.30	.30
Ethyl, 190 proof, bbls	gal.	4.75	4.75
Amyl Acetate	gal.	2.00	2.00



Courtesy of Drug & Chemical Markets

	Apr. 1	Apr. 15
Caffeine Alkaloid,..............lb.	3.75	3.75
Camphor, Jap, refined, cases.....lb.	.86	.82
Carbon Bisulfide, c/l............lb.	.06	.06
Tetrachloride..............lb.	.10	.10
Chloroform, U. S. P., drums......lb.	.37	.37
Creosote, U. S. P................lb.	.40	.40
Cresol, U. S. P..................lb.	.12	.13
Dextrin, corn..............100 lbs.	2.99	2.99
Imported Potato............lb.	$.08^{1}/_{2}$	.09
Ether, U. S. P., conc., 100 lbs....lb.	.14	.14
Formaldehyde, bbls..............lb.	$.08^{1}/_{2}$	$.08^{1}/_{2}$
Glycerol, dynamite, drums.......lb.	$.13^{1}/_{2}$	.13
Methanol, pure, bbls...........gal.	.75	.72
Methylene Blue, Med...........lb.	3.50	3.50
Petrolatum, snow-white.........lb.	$.12^{1}/_{2}$	$.12^{1}/_{2}$
Light Amber..............lb.	$.04^{1}/_{2}$	$.04^{1}/_{2}$
Green ....lb.	$.02^{3}/_{4}$	$.02^{3}/_{4}$
Pyridine......................gal.	1.75	1.75
Starch, corn, Pow'd.........100lbs.	2.32	2.32
Potato, Jap................lb.	.07	.07
Rice.......................lb.	.18	.18
Sago.......................lb.	.04	.04

OILS, WAXES, ETC.

	Apr. 1	Apr. 15
Beeswax, pure, white............lb.	.35	.35
Black Mineral Oil, 29 gravity....gal.	.22	.22
Castor Oil, No. 3................lb.	$.10^{1}/_{2}$	$.10^{1}/_{2}$
Ceresin, yellow. ....lb.	.08	.08
Corn Oil, crude, tanks, mills......lb.	.10	.10
Cottonseed Oil, crude, f. o. b. mill..lb.	.10	.10
Linseed Oil, raw (car lots)......gal.	.79	.83
Menhaden Oil, crude (southern).gal.	.40	.40
Neat's-foot Oil, 20°.............lb.	.24	.24
Paraffin, 128–130 m. p., ref.......lb.	.04	.04
Paraffin Oil, high viscosity.......gal.	.45	.45
Rosin, "F" Grade, 280 lbs.......bbl.	5.35	5.30
Rosin Oil, first run.............gal.	.36	.36
Shellac, T. N...................lb.	.78	.82
Spermaceti, cake................lb.	.30	.30
Sperm Oil, bleached winter, 38°..gal.	1.69	1 69
Stearic Acid, double-pressed......lb.	.10	$.09^{1}/_{2}$
Tallow Oil, acidless..............lb.	$.10^{1}/_{4}$	$.10^{1}/_{4}$
Tar Oil, distilled................gal,	.60	.60
Turpentine, spirits of...........gal.	.85	.86

METALS

	Apr. 1	Apr. 15
Aluminium, No. 1, ingots........lb.	.17	.17
Antimony, ordinary.........100 lbs.	4.35	4.50
Bismuth.........................lb.	2.10	2.00
Copper, electrolytic.............lb.	$.12^{3}/_{4}$	$.12^{3}/_{4}$
Lake......................lb.	$.12^{3}/_{4}$	$.12^{7}/_{8}$
Lead, N. Y......................lb.	.05	.05
Nickel, electrolytic..............lb.	.41	.41
Platinum, refined, soft...........oz.	90.00	90.00
Quicksilver, flask.........75 lbs. ea.	49.00	50.00
Silver, foreign ....oz.	$.64^{7}/_{8}$	$.65^{1}/_{2}$
Tin.............................lb.	$.29^{1}/_{4}$	.31

	Apr. 1	Apr. 15
Tungsten Wolframite.......per unit	2.00	2.00
Zinc, N. Y.................100 lbs.	5.00	5.10

FERTILIZER MATERIALS

	Apr. 1	Apr. 15
Ammonium Sulfate, export...100 lbs.	3.65	3.65
Blood, dried, f. o. b. N. Y.......unit	4.00	4.00
Bone, 3 and 50, ground, raw.....ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia......................	2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works......................unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:		
Florida Pebble, 68% ....ton	5.00	5.00
Tennessee, 78–80%...........ton	8.00	8.00
Potassium Muriate, 80%.......unit	.60	.60
Pyrites, furnace size, imported..unit	.14	.14
Tankage, high-grade, f. o. b. Chicago....................unit	3.25 & .10	3.50 & .10

COAL-TAR CHEMICALS

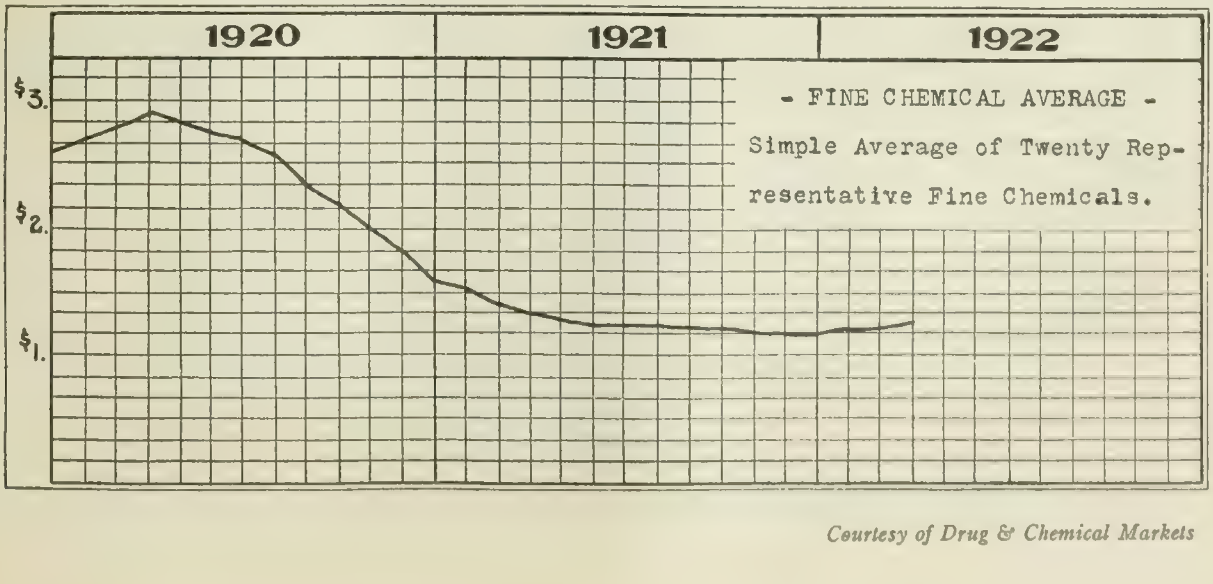
Crudes

	Apr. 1	Apr. 15
Anthracene, 80–85%............lb.	.75	.75
Benzene, pure, tanks ....gal.	.29	.29
Cresol, U. S. P..................lb.	.12	.12
Cresylic Acid, 97–99%..........gal.	.50	.50
Naphthalene, flake..............lb.	.07	.07
Phenol, drums..................lb.	.12	.12
Toluene, pure, tanks...........gal.	.30	.30
Xylene, 2 deg. dist. range, tanks.gal.	.45	.45

Intermediates

Acids:

	Apr. 1	Apr. 15
Anthranilic.................lb.	1.10	1.10
Benzoic tech...............lb.	.50	.50
Broenner's.................lb.	1.55	1.55
Cleve's....................lb.	1.50	1.50
Gamma.....................lb.	1.90	1.90
H.........................lb.	.85	.85
Metanilic..................lb.	1.00	1.00
Monosulfonic F.............lb.	2.30	2.30
Naphthionic, crude..........lb.	.65	.65
Nevile & Winther's..........lb.	1.25	1.25
Phthalic...................lb.	.32	.32
Picric.....................lb.	.20	.20
Sulfanilic..................lb.	.22	.22
Tobias'....................lb.	1.50	1.50
Aminoazobenzene...............lb.	1.15	1.15
Aniline Oil.....................lb.	$.15^{1}/_{2}$	$.15^{1}/_{2}$
Aniline Salt....................lb	.24	.22
Anthraquinone..................lb.	1.40	1.40
Bayer's Salt ....lb.	1.00	1.00
Benzaldehyde, tech ....lb.	.55	.55
U. S. P...................lb.	1.40	1 40
Benzidine (base)................lb.	.85	.85
Benzidine Sulfate...............lb.	.70	.70
Diaminophenol..................lb.	5.50	5.50
Dianisidine.....................lb.	4.75	4.75



Courtesy of Drug & Chemical Markets

		Apr. 1	Apr. 15
p-Dichlorobenzene	lb	.17	.17
Diethylaniline	lb.	.60	.60
Dimethylaniline	lb	.36	36
Dinitrobenzene	lb.	.20	.20
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.60	.60
G Salt	lb.	.65	.65
Hydroquinol	lb.	1.35	1 35
Metol (Rhodol)	lb	3.50	3.50
Monochlorobenzene	lb.	.10	.10
Monoethylaniline	lb.	1.00	1.00
a-Naphthylamine	lb.	.30	.30
b-Naphthylamine (Sublimed)	lb.	1.50	1.50
b-Naphthol, dist	lb.	.28	.28
m-Nitroaniline	lb.	.77	.77
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.09	.09
Rectified (Oil Mirbane)	lb.	.10	.10
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	—	—
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.70	.70
m-Phenylenediamine	lb	1.05	1.05
p-Phenylenediamine	lb	1.50	1.50
Phthalic Anhydride	lb.	.35	.35
Primuline (Base)	lb.	2 00	2.00
R Salt	lb.	60	.60
Resorcinol, tech	lb	1.50	1.50
U. S. P	lb	1.75	1.75
Schaeffer Salt	lb	.70	.70
Sodium Naphthionate	lb	.70	70
Thiocarbanilide	lb.	.37	.37
Tolidine (Base)	lb	1.20	1.20
Toluidine, mixed	lb	.30	.30
o-Toluidine	lb	.20	.20
p-Toluidine	lb	1.00	1.00
m-Toluylenediamine	lb	1.05	1.05
Xylidine, crude	lb	45	.45

COAL-TAR COLORS

Acid Colors

		Apr. 1	Apr. 15
Black	lb.	.80	.80
Blue	lb	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III	lb	.50	.50
Red	lb.	.85	.85
Alkali Blue, domestic	lb.	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	6.00	6.00
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Apr. 1	Apr. 15
Black	lb	.55	.55
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	2.00	2.00
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb	1.10	1.10
Congo Red, 4B Type	lb	.90	.90
Primuline, domestic	lb	1.75	1.75

Oil Colors

		Apr. 1	Apr. 15
Black	lb	.70	.70
Blue	lb.	1.25	1.25
Orange	lb	.95	.95
Red III	lb	1.65	1.65
Scarlet	lb	1.00	1.00
Yellow	lb	1.25	1.25
Nigrosine Oil, soluble	lb	.90	90

Sulfur Colors

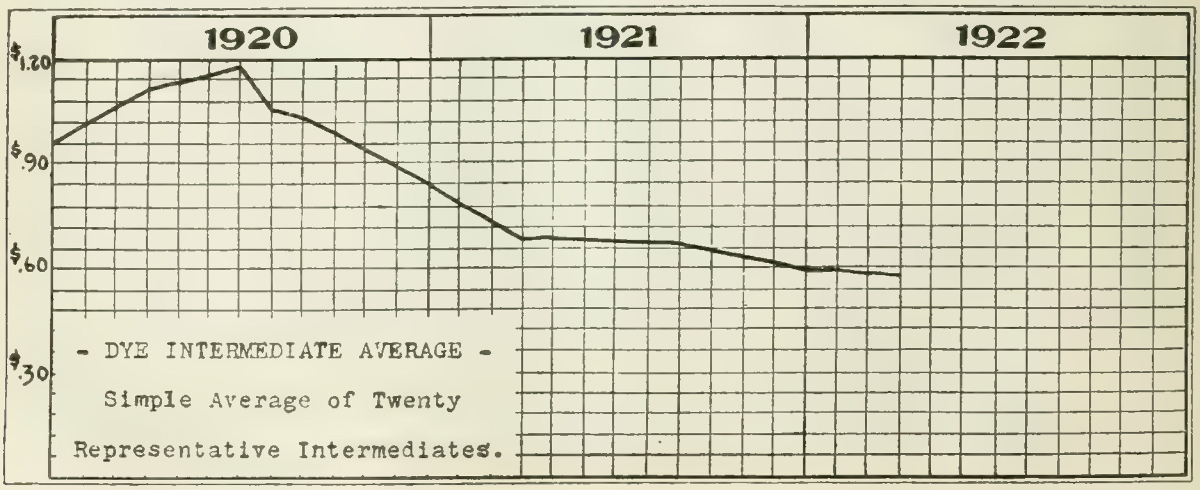
		Apr. 1	Apr. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.60	.60
Brown	lb.	.35	.35
Green	lb	1.00	1.00
Yellow	lb	.75	.75

Chrome Colors

		Apr. 1	Apr. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb	.85	.85
Chrome Black, domestic	lb.	.55	.55
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb	1.50	1 50
Chrome Red	lb.	1.75	1 75
Gallocyanin	lb.	2.30	2 30

Basic Colors

		Apr. 1	Apr. 15
Auramine, O, domestic	lb	1.50	1 50
Auramine, OO	lb.	2.50	2 50
Bismarck Brown R	lb	.70	70
Bismarck Brown G	lb.	1.00	1 00
Chrysoidine R	lb.	.75	75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	2.25	2 25
Indigo, 20% paste	lb.	.45	45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2 00
Malachite Green, crystals	lb.	1.60	1.60
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc	lb.	8.00	8.00
Victoria Blue, base, domestic	lb.	3.50	3.50
Victoria Green	lb.	1.50	1.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00



Courtesy of Drug & Chemical Markets

The Journal of
INDUSTRIAL & ENGINEERING CHEMISTRY
Published Monthly by The American Chemical Society

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New York City
TELEPHONE: Gramercy 2145

Volume 14 JULY 1, 1922 No. 6

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EDITORIALS

Patent Progress

WHEN the Patent Committee reported in 1921, the Council voted "that a constructive suggestion should be made by the Committee as to legislation which would prevent the utilization of our patent office by foreigners for the suppression of the development of industries." At the request of Mr. E. J. Prindle, Chairman of our Patent Committee, President Smith called a meeting of the Committee on National Policy on May 13. Mr. Prindle discussed the Stanley Bill and its undesirable features. Mr. Henry Howard, President of the American Institute of Chemical Engineers and member of the National Industrial Conference Board, presented the Stanley Bill as amended. After an extended discussion, the Committee in executive session unanimously adopted the following resolution:

> In the opinion of the AMERICAN CHEMICAL SOCIETY, our patent system was designed primarily to encourage industry in the United States as well as to reward inventors. When any patentee, whether domestic or alien, uses his patent to smother or limit an industrial development in the United States, he is to that extent defeating the purpose of the patent law.
>
> *Therefore*, the AMERICAN CHEMICAL SOCIETY puts itself on record as being in favor of the principle of the Stanley Bill, S. 3410, as amended April 20 (Calendar day, May 4), 1922, and suggests that in any modification of the wording thereof, found desirable by the Committee, they consider the public welfare and the national defense of equal importance.

The amendment to the Stanley Bill provides that if a United States patent is worked abroad but not in this country, two years after its issuance, and if the patentee has refused to grant licenses upon reasonable terms for its practice in this country, the U. S. Court of Appeals may order a nonexclusive license granted. As now worded, the bill applies only to American patents which are also taken out in foreign countries (less than ten per cent), and affords protection to the patentee during the developmental period through a recognition of ability to prove reasonable diligence in bringing about a bona fide working of the patent.

While the chemical industry considers a general working clause undesirable, there is agreement that not only the chemical industry but other industries require protection against the smothering of industrial development which has been effected through the protection afforded by our patent system. No one wishes to see the benefits of the American patent system destroyed, but some way must be found whereby those who manufacture abroad and patent in this country solely for the purpose of preventing competition from American-made goods may be denied such opportunity. This amendment is believed to offer a solution of the problem. Chemists should urge its adoption.

Future Plans

OUR September issue will be a progress number. We have been assured of the active coöperation of a large number of specialists who will prepare short summaries of the advance made in scientific research and technical development in their fields of work. Later, we shall have other numbers largely devoted to articles of this type, which will enable those not specializing in a particular field to learn, in a few minutes' reading, the status of a great many different activities.

The Committee of Seven

UPON several occasions very busy members of the AMERICAN CHEMICAL SOCIETY have been put upon committees to consider difficult problems and to recommend procedure to the SOCIETY. We know of several cases where the conscientious work performed involved an inordinate amount of time and personal expense, while the SOCIETY chose to make no use of the results. We hope that the committee appointed by President Smith on Progress in Society Procedure may not have a similar experience.

Great scientific societies, like business enterprises, must occasionally take stock and decide whether they are proceeding along the best possible lines. A number of American chemists have expressed the belief that the SOCIETY should now review its activities, the functions of its various committees, and its methods of procedure, and decide upon what changes, if any, should be made to enable it better to advance the interests of chemistry, the chemical profession, and the chemical industries in our country. The Committee is as follows:

A. V. H. Mory, 565 W. Washington St., Chicago, Ill., *Chairman*, has performed service in the laboratories of the Government, in industry, and as a consultant.

George L. Coyle is Professor of Chemistry, Holy Cross College, Worcester, Mass.

L. C. Drefahl is Chairman of the Cleveland Section, and an official of the Grasselli Chemical Company.

Graham Edgar is Professor of Chemistry, University of Virginia.

H. C. Parmelee is Editor of *Chemical and Metallurgical Engineering*.

J. N. Swan is Professor of Chemistry at the University of Mississippi.

R. E. Swain hails from California, from Stanford University. He will be able to bring to the committee the views of many far-western chemists who seldom have the privilege of attending the meetings of the SOCIETY.

Surely anyone who has given much thought to the problems before the Committee can express his views in extenso to that member of the Committee best known to him, or the one most accessible.

Let us as members of the SOCIETY do our part toward making the present work thorough, satisfactory, and adequate.

The Tariff Status

THE strongest opponents of the chemical embargo have testified that under the present arrangement monopolies have not been formed, price agreements have not been made, the industry has developed beyond the greatest expectations, and under it continued growth may be expected. The embargo is to continue until some definite action is taken with respect to the tariff. Chemical manufacturers might be less interested in the present leisurely congressional procedure but for the uncertainty which hangs over them.

Seldom has the need been emphasized for men in Congress capable of visualizing what is best for the country as a whole, as opposed to the usual trading policy in which the interest of a comparatively small group of constituents is paramount. Fortunately, Congress has at its command the services of men who are specialists, but in addition to the advice of specialists we need men capable of understanding the advice when given and able to steer a course with the welfare of the people as a whole as the only goal. With increasing complexity of modern industrial affairs involving new sorts of trade and commerce, bringing us into competition with an increasing number of foreign countries, difficulties with foreign exchange, and all that, we have not commanded for government service men who have grown with the job.

From the senatorial discussion of acetic anhydride we might conclude that this was prepared from acetic acid by the simple process of removing water with filter paper. So great an amount of time is spent in arguing points not understood that there is reason to suspect certain senators of filibustering with the purpose of embarrassing the Administration in the November elections.

Much industrial development is waiting on tariff legislation. In the hope that something may be done this year, Congress has been holding night sessions, but on the 16th the usual night session was omitted to permit the pages of the Senate, as guests of Senator Elkins, to attend the circus then in Washington!

To some men political power is always paramount to national welfare. They do not hesitate to follow tactics detrimental to our industrial interests if by that means they may win reëlection or, failing that, continue to have their party hold its place. Every experiment with tariff bill making convinces a greater number of thoughtful people that the tariff must be taken out of politics and placed upon a scientific and economic basis. We can but exclaim with the prophet of old, "O Lord, how long?"

American Chemical Literature

In the February number of This Journal, under the caption "Criticism from Germany," Dr. W. A. Noyes called attention to the attitude of certain foreign scientists regarding the upbuilding of American chemical literature. The fears of our critics are well founded if the success of the monograph series is indicative of the future. There has been no better example of what American chemists can accomplish through organization, confidence in an idea, and faith in their leaders. If there be any who still favor former sources for literature, let them consider the last edition of Beilstein. There are to be seventeen volumes. To those who subscribed for the set, volumes one and two were sold for $12 for the two. Volume three has appeared at $18, and it is understood that volume four will cost about $28. Volume seventeen?

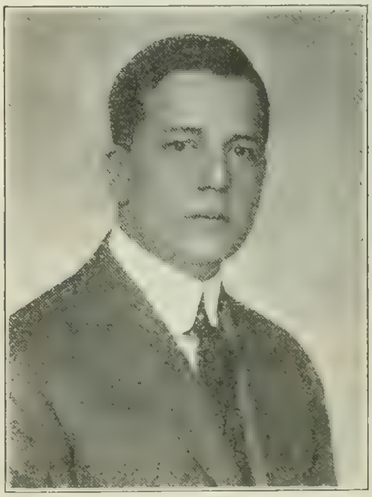
Americans can compile reference works and write texts using the same sources as have the others. They can do a better job because they know American needs.

Our monographs are already a success. Six volumes are now in circulation, and the seventh will appear this month. It is believed that at least eight more will appear before January 1, 1923. Twenty are in preparation, and the editors still seek monographs of the type that deserve a place in this remarkable series. Of the books published, several thousand volumes have been sold, and of those to come orders have been placed for a still larger number. The majority of the books published have already paid the royalties advanced to authors, and have begun to earn a profit for the authors, the Society, and our loyal publishers. Some of the monographs have been undertaken because their type of book is needed, rather than because all can have the same wide sale.

The series presents a great opportunity to authors, but it involves responsibility. Unforeseen circumstances may alter the best laid plans. When, however, an author undertakes a monograph and the subject is announced, the public quite correctly expects the author to give them the benefit of his special knowledge and information at as early a date as possible. Then, when the monograph, carefully reviewed by authorities before its publication, appears, we chemists should get behind it and do what we can toward making its distribution completely successful.

We should remember that the monograph venture was not undertaken for profit, but primarily to create a nucleus for chemical literature in English without the usual commercial considerations. Any enterprise which the members of the Society wish to back with their individual interest and the weight of their organization will be a certain success. Individual members should be eager to contribute whatever they can to a speedy realization of the great promise of future success. American chemists can guarantee an American chemical literature.

Meet Mr. Stokes



On May 15 Mr. R. T. Stokes became the Associate Editor of This Journal. His headquarters are at One Madison Avenue, New York City. Mr. Stokes comes to us from Chicago, where until recently he was a member of the technical staff of Sears, Roebuck & Co. He is a graduate of Dartmouth, has taught at Hobart College, and has been assistant to Professors Baskerville and Moody at the College of the City of New York. In industrial work he has been particularly interested in rubber, and during 1917 was superintendent of the rubber factory of Parker, Stearns & Company, Brooklyn, N. Y.

Mr. Stokes will not only represent the Journal in New York but will be found about the country, endeavoring to find ways of making This Journal of still greater service to the chemical industry.

Earning Power of Research

In discussing the fact that a patent is not necessarily a complete exposure of chemical processes and products, Mr. Henry Howard, Vice President of the Grasselli Chemical Company, related his experience in the production of stable hydrosulfite.

Foreign patentees would license no one to make stable hydrosulfite, but when it became possible to obtain a license from the Chemical Foundation, the Merrimac Chemical Company began work. In the laboratory it was found that notwithstanding faithful adherence to the methods prescribed in the patents, stable hydrosulfite was not forthcoming, and the entire venture would have failed but for research. Research upon the composition of the original material, involving microanalysis, disclosed impurities which furnished the clue. After nine months' intensive work, the research laboratory solved the problem and production was successful.

SYMPOSIUM ON DISTILLATION

Papers presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

The Efficiency and Capacity of Fractionating Columns

By **W. A. Peters, Jr.**

E. I. du Pont de Nemours & Co., Wilmington, Delaware

The capacity of a fractionating column is defined as a measure of the amount of vapor and liquid which can be passed countercurrent to each other in a column without causing the column to load or prime. The efficiency is defined as the separating power of a definite unit or length of the column and is measured by comparing its performance with the performance calculated for a theoretically perfect plate column under similar conditions.

Plate Columns

The theoretically perfect plate column has been defined by Professor Lewis and from his definition it follows that

$$X_{n+1} = \frac{Y_n - Y_c(1-\rho)}{\rho} \qquad (1)$$

where

X_{n+1} = the equivalent latent heat fraction of the low boiling material in the liquid on the $(n+1)^{th}$ plate.
Y_n = equivalent latent heat fraction of the low boiling material in the vaporizing from the n^{th} plate.
Y_c = equivalent latent heat fraction of the low boiling material in the distillate.

By equivalent latent heat fraction is meant the heat required to volatilize the amount of low boiling material in 1 lb. of the mixture on or above the given plate divided by the latent heat required to volatilize one pound of this mixture. Expressing the compositions in this way simplifies the calculations.

ρ = the ratio of the heat required to volatilize the liquid run back divided by the total latent heat in the vapor passing up through any horizontal cross section of the column. This is also often called the reflux ratio. These relations are of course true only when radiation and changes in heat content of the liquid are neglected over the section of column considered.[1] Formula 1 gives the relation which must exist between the compositions of the vapor rising from one plate, the liquid refluxing from the plate above, and the heat balance in the theoretical column. If ρ, Y_c and Y_n are known, X_{n+1} can be determined, Y_{n+1} will then be fixed, according to the definition of the theoretical column, and thus the composition of the liquid and vapor at every point in the theoretical column will be fixed. (Fig. 1.)

To compare an actual column with the theoretical column, then, it is necessary to run the column on some given mixture and to measure ρ, Y_n and Y_c. The theoretical column which will give the same values for Y_n and Y_c with the same value for ρ is then calculated, and the number of plates so calculated divided by the number of plates actually employed to make the separation gives the efficiency factor, K, of the actual column. If the column tested is a filled column, the number of plates in the calculated theoretical column divided by the height of the filled column in any units chosen gives a measure of the efficiency of the filled column. We have found it convenient to measure the reciprocal of this efficiency, which will be called the "height of equivalent theoretical plate," or H. E. T. P.

SIEVE TYPE—An example will be given as an illustration of the method.

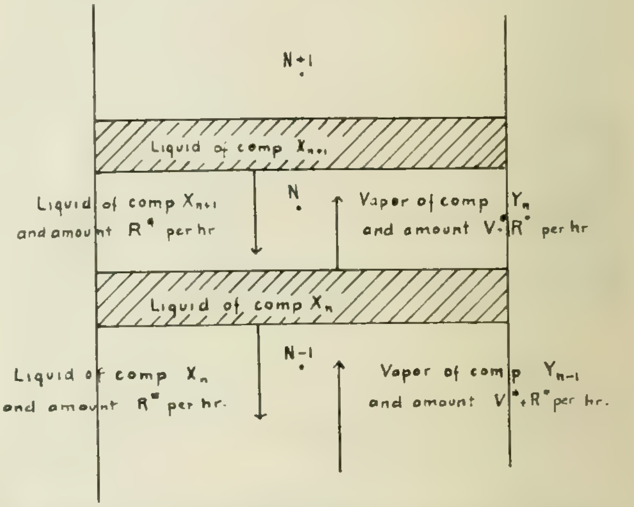

N+1
Liquid of comp X_{n+1}
N
Liquid of comp X_{n+1} and amount R^* per hr
Vapor of comp Y_n and amount $V^* + R^*$ per hr
Liquid of comp X_n
N-1
Liquid of comp X_n and amount R^* per hr.
Vapor of comp Y_{n-1} and amount $V^* + R^*$ per hr.

Fig. 1 Diagram of Plates of Theoretical Column for Materials with Equal Latent Heats

Example

The column tested was a 28-in. diameter sieve plate column with twenty-eight plates separating acetic acid and water.

The following data were obtained:

Vapor from still	70.8 per cent water
Distillate	98.52 per cent water
Liquid on top plate	98.14 per cent water (from curve)
Steam condensed in coil	1980 lbs. per hr.
Distillate	200 lbs. per hr.

The latent heat of acetic acid will be taken as 90 and that of water as 540.

$$\text{Then } Y_S \text{ (vapor from the still)} = \frac{70.8 \times 540}{70.8 \times 540 + 29.2 \times 90} = 0.935$$

$$Y_C \text{ (distillate)} = \frac{98.52 \times 540}{98.52 \times 540 + 1.48 \times 90} = 0.998.$$

Total heat in vapor passing up column (available heat in 1980 lbs. steam condensed under pressure at 500 P. C. U. per lb.) = 990,000 P. C. U.

Heat to vaporize 200 lbs. of distillate containing 98.52 per cent water and 1.48 per cent acetic acid = 108,000 P. C. U.

$$\text{Then } \rho = 1 - \frac{108{,}000}{990{,}000} = 0.89$$

$$\text{Hence } X_1 = \frac{0.935 - 0.998\,(1-0.89)}{0.89} = 0.927$$

which calculated back to actual percentage is 67.8 per cent water. From the known relations between the compositions of the vapor and liquid phases of acetic acid and water mixtures at equilibrium, the value of Y_1 for X_1 = 67.8 per cent is found to be 76.1. X_2, etc., are then calculated in the same way, until finally X_{15} is found to be 98.1. The results of the calculations are shown in Table I.

Of course the work can be simplified by expressing all compositions and amounts as equivalent heat fractions and drawing all curves in the same terms, just as for some purposes it is found convenient to express relationships in terms of molal fractions, or Formula 1 can be so written that compositions and amounts are expressed in actual percentages and pounds in which case it becomes:

---

[1] If $\rho = \frac{R_{n+1}}{R_{n+1}+V_c}$, Formula 1 may be written $R_{n+1} = \frac{V_c(Y_c - Y_n)}{Y_n - X_{n+1}}$.

$$X_{n+1} = \frac{Y_nL_c - Y_c(1-\rho)L_n}{L_c - (1-\rho)L_n}$$

where

L_c = latent heat of distillate of composition Y_c, and
L_n = latent heat of vapor of composition Y_n.

TABLE I

PLATE	COMPOSITION OF LIQUID Per cent Water	VAPOR Per cent Water
Still	77.9	70.8
1	68.4	76.1
2	74.2	80.4
3	78.5	83.6
4	82.1	86.2
5	85.0	88.4
6	87.1	90.0
7	89.0	91.5
8	90.8	93.0
9	92.5	94.3
10	93.8	95.3
11	95.0	96.2
12	96.0	97.0
13	96.9	97.6
14	97.6	98.2
15	98.1	98.6

Thus approximately fifteen plates of the theoretical column are required to do the work of the sieve plate column with twenty-eight plates, making the average value of K for the sieve plate column

$$15/28 = 0.536.$$

Other tests made on several different sieve plate columns with acetic acid and water mixtures gave the following values for K:

$K = 0.538$ $\rho = 0.82$
$K = 0.500$ $\rho = 0.84$
$K = 0.500$ $\rho = 0.87$

It was proved by these tests, checked by many others on packed columns, that for acetic acid and water mixtures in sieve plate columns with about 1-in. depth of liquid on the plates, K is independent of ρ within the limits 0.8 to 1.0, and also of the composition of the reflux or the vapor. The mean value for K, then, for 1 in. of liquid on plates and perforations of about 0.2-in. diameter, is 0.52.

BUBBLER CAP TYPE—Tests made on a standard 36-in. diameter Badger bubbler cap plate column with alcohol-water mixtures containing less than 90 per cent alcohol by weight gave a value of 0.70 for K. For mixtures richer in alcohol the value of K is less. This higher efficiency of the bubbler cap column on alcohol-water mixtures was surprising and could not easily be accounted for.

To prove whether it was due to a difference between the two types of columns, sieve or bubbler cap, or to a difference in the behavior of the two mixtures, two tests were made in which acetic acid and water, and alcohol and water, were run in the same bubbler cap plate column under exactly similar conditions. The column used was $4^7/_8$ in. inside diameter and had one bubbler cap 2 in. in diameter per plate. The immersion of the slots was only 0.25 in., though their width was $^1/_{16}$ in., so that if there was a difference in K for the two mixtures we would expect it to be accentuated in this small column. The column had twenty plates, and samples were taken from the first, sixth, eleventh, sixteenth, and twentieth plates and from the distillate. K was found to be 0.45 for the acetic acid and water and 0.694 for the alcohol and water below the sixteenth plate. Above the sixteenth plate K could not be accurately determined for the alcohol.

This test indicates that there is no difference between the efficiency of plate columns of the sieve or bubbler cap type, provided the immersion and diameter of the slots or perforations are comparable.

But there is a marked difference in the efficiency of the same column for different mixtures. An even greater difference was found when we came to study packed columns.

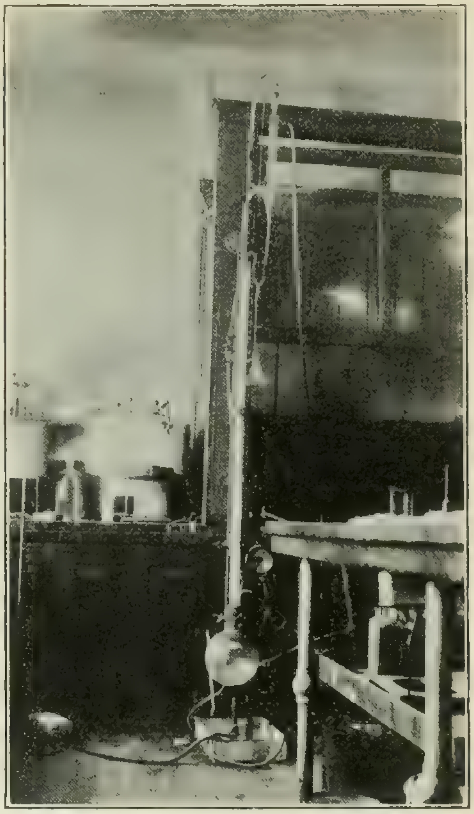


FIG 2

Some work on plant columns had indicated this, so the apparatus shown in Fig. 2 was set up, and the height of 0.25-in. ring filling equivalent to one theoretical plate (H. E. T. P.) was determined for many different mixtures.

The method of determining this H. E. T. P. was exactly the same as used to determine the efficiency of the 28-plate sieve plate column. A separation was made under given conditions, and the number of plates in the theoretical column required to make the same separation was calculated. The height of filling used divided by this number gave the H. E. T. P.

The values found for 0.25-in. fillings are shown in Table II.

TABLE II

MATERIALS SEPARATED	H. E. T. P. In.	Comparative Efficiency Alcohol-Water below 88 Per cent = 100
Ethyl alcohol + water below 88%	3.65	100
Ethyl alcohol + water above 88%	4.2	87
Methanol + water	3	122
Acetone and ethyl alcohol	6	61
Nitric acid + water	8	46
Acetic acid + water	10	36
Benzene + toluene	10	36

Next the apparatus shown in Fig. 3 was run as an exhausting column.

The values for the H. E. T. P. are shown in Table III.

TABLE III

MATERIAL	H. E. T. P. In.	Comparative Efficiency
Ethyl alcohol + water	3.87	94
Ammonia + water	3.4	107
Nitric acid + water and sulfuric acid	3.75	97

From the fact that ethyl alcohol-water and acetic acid-water mixtures are at about the extremes in these tables, the conclusion is drawn that in well-constructed plate columns K, for most materials, will lie between the values found for these two mixtures, *i. e.*, 0.5 and 0.7. We have some confirmation of this in a test on materials boiling around 200° C. which were fractionated in a 4-ft. diameter, 30-plate, cast-iron, bubbler cap column and gave a value for K of about 0.5.

Fig. 3

Some general predictions can be made about the value of K on the basis of these figures.

1—K is less for materials of high molecular weight.

2—For materials of equal molecular weight those mixtures in which there is less attraction between the unlike than between the like molecules will show the higher value of K.

The latter point is especially well brought out in the case of nitric acid and water mixtures. The addition of sulfuric acid, which is known to decrease the attraction of the nitric acid for the water, changes the H. E. T. P. from 8 in. to 3.75 in.

It is thus seen that the efficiency of a given column varies as it is used to separate different mixtures. From an engineering standpoint, the question is how to increase the efficiency of the column for all mixtures. With plate columns this can be done by increasing the immersion and decreasing the diameter of the slots or perforations. Either change increases the resistance to vapor passage through the column and hence increases the back pressure at the base of the column. Probably 1-in. immersion and 0.2-in. diameter slot is about the best design; for these figures K will vary from about 0.5 to a little over 0.7. It is doubtful if K could be increased much above these figures without causing excessive pressures on the still.

Packed Columns

In the case of packed columns the reciprocal of K, or the H. E. T. P., is found to vary nearly directly with the mean diameter of the filling pieces. Fig. 4 shows this relation for acetic acid and water mixtures.

It is evident that columns filled with very small pieces can be extremely short to make a given separation. The serious objection to the smaller fillings is their cost.

In order to find the cost of a packed column we must know the diameter or cross-section area as well as the height. The factor which determines the diameter will be called the capacity factor and will be measured by the cross-section area of the given column required to pass 1 cu. ft. of the vapors to be separated per second. This factor multiplied by the H. E. T. P. gives a volume which will be called the volume efficiency factor and which measures the relative over-all efficiency of any column packing, or of any column, in fact. To compare columns, then, we can reduce all costs to the basis of cost per unit volume efficiency factor. This simplification is useful only in special cases, because it does not take into consideration differences in height. For purposes of practical design, it is more convenient to work with a simple capacity factor which we measure by the maximum vapor velocity which the given column will stand without priming. Fig. 5 shows this velocity for several types of filling materials. It will be noted that the maximum vapor velocity has been determined for different reflux ratios and that the values of L/V (liquid refluxed divided by vapor passing up the column) lie on parallel straight lines in the region studied. To make the results comparable the vapor is expressed as lbs. of water vapor which have a latent heat equivalent to the latent heat of the vapor actually passing up the column.

An interesting comparison of the relative capacities and efficiencies of different shaped filling materials is shown in Table IV.

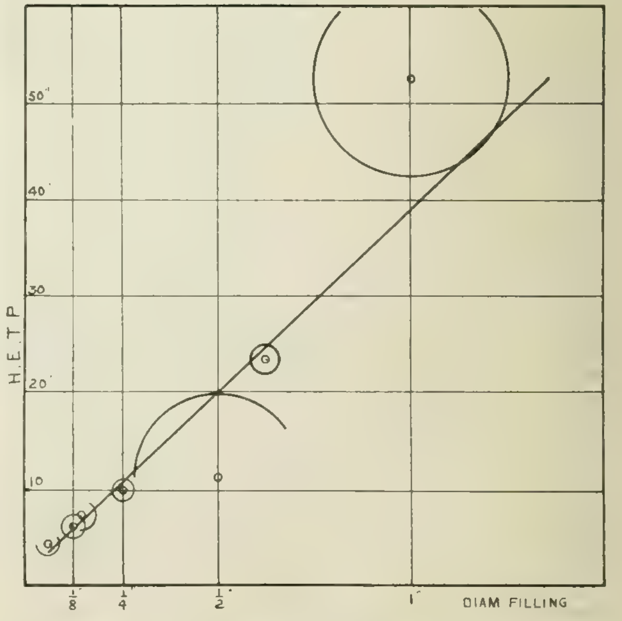


Fig. 4—Efficiency of Fillings of the Hollow Ring Type on Mixtures of Acetic Acid and Water

The Larger Circles Represent the Probable Error of the Determinations

TABLE IV

FILLING	Relative Free Space	Relative Capacity	Relative Efficiency	Relative V. E.
0.25-in. hollow cylinders	100 actual 71%	100	73	73
0.25-in. solid spheres	57	About 70	100	70
0.25-in. solid cylinders	54	54	About 73	40
0.75-in. copper nails	100	140	...	..

The maximum over-all vapor velocities calculated over the whole cross section of the column for different columns with various materials is shown in Table V.

TABLE V

MIXTURE	COLUMN OR FILLING	M. V. V. Ft. per sec.	REMARKS
Benzene + toluene	Bubbler cap	1.2	Column not quite to capacity
Alcohol + water		1.3	
High boilers under high vacuum		4 to 5	
Ether, alcohol + water		1.0	Column not quite to capacity
Acetic acid + water, weak	Sieve plate	3.1	
Acetic acid + water, strong		1.25	
Alcohol + water, weak, in beer still		3.0	
Acetic acid + water, weak	0.25-in. rings	4.4	
Acetic acid + water, strong		2.0	
Alcohol + water, weak		3.37	
Alcohol + water, strong		About 2.5	

The great advantage of columns packed with the small rings is apparent from this table and from Table II. Columns filled with them will in general be shorter and of less diameter than equivalent plate columns.

The only question is the cost of the small packing. We have proved that an irregular filling such as pebbles or broken quartz will have a low capacity. The small hollow cylinders make an ideal filling material provided their cost is not excessive. The Hydronyl Syndicate of London has offered 0.25-in. copper or aluminium contact rings for about $250 per cu. ft.[1] We have devised and are applying for a patent on a method by which we can make hollow cylinders 0.25 to 0.375 in. in diameter for about one-eighth the previous figure.

RELATIVE COST OF COLUMNS

As an example of the method of comparison and to show the relative costs of the two types of columns let it be required to design a cast-iron, bubbler cap plate column and a column packed with 0.25-in. cylinders, each to be equivalent to fourteen theoretical plates and to deliver 41 gal. of 92.5 per cent alcohol per hr. with an average value of 0.8 for ρ.

The total vapor to be passed up the column will be

$$\frac{41 \times 6.8 \times 10.5}{0.2 \times 3600} = 4.1 \text{ cu. ft. per sec.}$$

From Table V it is seen that the maximum vapor velocity for the plate column is 1.3 and for the packed column 2.5 ft. per sec. Therefore, the diameter of the plate column must be 24 in. and of the packed column 18 in.

K for the plate column is 0.7, so twenty plates will be required. For the packed column, the H. E. T. P. will be taken as 4 in., making it $\frac{14 \times 4}{12} = 4.7$ ft. high. To this height will be added a foot to allow for distribution of liquid at the top of the column.

A cast-iron column 24 in. in diameter with twenty plates actually cost $1300 in 1919 and could probably be made now for $1000.

The cost of the packed column will be

10 cu. ft. of filling at $30.00 per cu. ft. (estimated)	$300.00
Shell, 6 ft. of 18-in. cast-iron pipe	25.00
Top and bottom flanges	15.00
Support for filling	25.00
TOTAL....	$365.00

The packed column is thus cheaper and shorter than the plate column.

In the case of columns used for acetic acid-water separations it is estimated that a column 25 in. in diameter with twenty-eight sieve plates will cost $1350. An equivalent packed column filled with 0.25-in. cylinders at the low cost for which we expect to make them, will cost about $1200. The first cost of the packed column is not so much lower in this case, but its life should be much longer than that of the plate column.

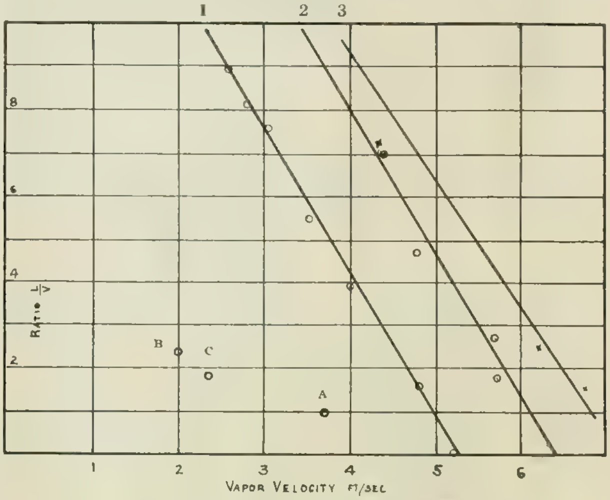


FIG. 5—CAPACITY OF FILLED COLUMNS

1—0.25-in hollow cylinders, water; 2—0.5-in. hollow cylinders, water; 3—0.75-in. copper nails, A—0.25-in. lead shot; B—0.25-in. hollow cylinders, strong acetic acid; C—0.25-in. hollow cylinders, strong ethyl alcohol

Of course there are many cases where packed columns cannot be used and some cases where plate columns would not be practicable. Each case must be considered separately. Many problems cannot be solved exactly; for instance, to calculate the column required for separating the impurities from a crude methanol would be nearly impossible. But even where no definite calculations can be made, the method outlined by Professor Lewis and the data we have given should be of some help in designing a distillation plant, especially where it is possible to make preliminary experiments on a laboratory or semiworks scale. By the method outlined it is possible to make direct comparisons between laboratory and plant fractionating columns and to design a large column to make any desired separation that has been made in a laboratory column.

SUMMARY

The method described by W. K. Lewis for measuring the efficiency of a fractionating column has been applied to plate columns of both sieve and bubbler cap type, and to packed columns. The efficiency of plate columns of either type was found to be the same for a given separation. The efficiency of packed columns was found to vary inversely as the diameter of the packing pieces. The efficiency of any column was found to depend on the materials being separated.

The capacity of the columns was also determined and a method for figuring the comparative cost of columns for a given separation was developed.

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[1] These rings, patented by Dr. R. Lessing, are described by him and some qualitative data are given on their performance, *J. Soc. Chem. Ind.*, **40** (1921), 115.

The Plate Efficiency of a Continuous Alcohol Still[1]

[ABSTRACT]

By Clark S. Robinson

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

THREE tests on a continuous alcohol still under varying conditions indicated average plate efficiency of from 24 to 56 per cent.

The equations developed by W. K. Lewis for the calculation of the number of plates for a fractionating column[2] require two things for their use, first, the relation between the vapor and liquid compositions, and, second, the plate efficiency. Up to the present time nothing regarding the latter has been available in the literature.

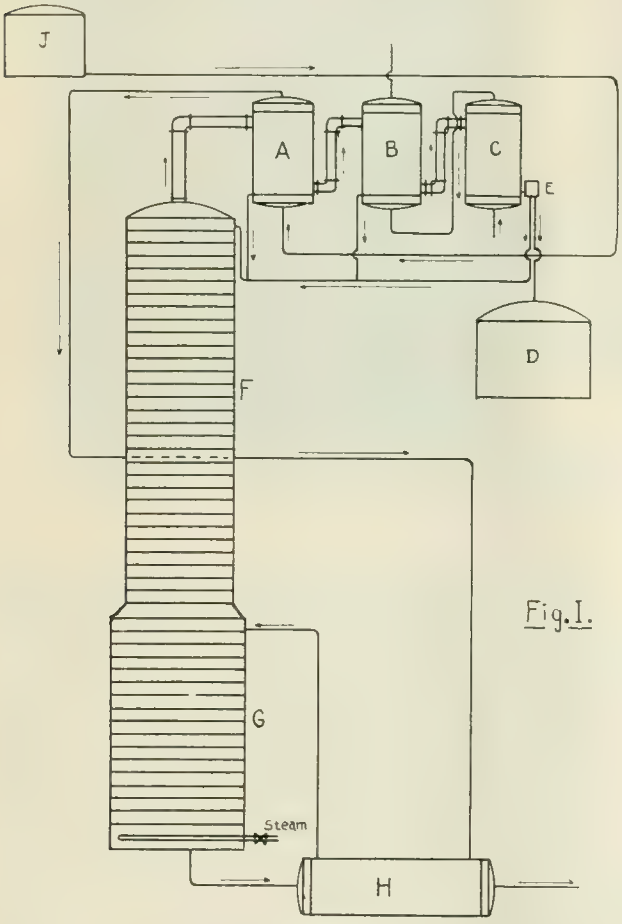

Fig. I.

The writer has obtained three careful tests on a continuous still handling ethyl alcohol-water mixtures. This still is of the modern Barbet type with plates fitted with boiling caps as described by Barbet[3] and by Mariller.[4] The still is illustrated in Fig. 1.

It consisted of a rectifying column, F, of 30 plates, 1.52 m. in diameter and an exhausting column, G, of 16 plates, 1.65 m. in diameter. The dilute alcohol was taken from a feed tank, J, through condenser A where it was partly heated, then to a heat interchanger, H, where it was heated nearly to the boiling point, and was then delivered on to the top plate of the exhausting column.

The vapor leaving the top of the rectifying column was partly condensed in the condensers A and B, and the residual vapor was totally condensed in the condenser C. The liquid from condensers A and B and a portion of that from C was returned to the top of the rectifying column as reflux, the remainder of that from C being withdrawn through suitable coolers to the receiver D. Cooling water flowed through condensers C and B in series.

The averaged data on an hourly basis are listed in Table I:

TABLE I

Test number	1	2	3
Alcohol fed, kg.	623	772	818
Water fed, kg.	491	591	636
Cooling water, kg.	13600	13250	13000
Water indistillate, kg.	45	68	59
Rise in temperature of feed in condenser A, ° C.	45.2	43.3	42.3
Rise in temperature of water in condenser B, ° C.	27.9	26.3	26.0
Rise in temperature of water in condenser C, ° C.	25.5	29.0	27.2

In all cases the amount of alcohol in the waste was too small to be measured.

It was found possible to determine the average plate efficiency of the still for these tests by means of the equations:

$$\frac{dx}{dn} = k\,(y_n - x_n) - \frac{k}{R_n}\,(y_c - y_n) \text{ for the rectifying column and}$$

$$\frac{dn}{dm} = k\,(y_m - x_m) - \frac{k\,(R_f - 1)}{R_m}\,(y_m - x_w) \text{ for the exhausting column,}$$

these equations having the significance indicated in the abovementioned paper.[2]

TABULATED CALCULATIONS

Test number	1	2	3
Kg. moles alcohol in product	13.5	16.7	17.7
Kg. moles water in product	2.5	3.97	3.28
Mole fraction alcohol in product	0.842	0.816	0.844
Heat removed in condenser C (Kal.)	346,000	384,000	354,000
Heat removed by product (ML = 9,500) (Kal.)	153,000	195,000	200,000
Heat removed by reflux from condenser C.	193,000	189,000	154,000
Moles reflux from condenser C	20.3	19.8	16.1
Heat removed in condenser B (Kal.)	379,000	249,000	339,000
Moles reflux from condenser B	39.9	36.7	35.5
Heat removed in condenser A (Kal.) (C_p = 0.95)	48,000	56,000	58,000
Moles reflux from condenser A	5.05	5.9	6.1
Total moles reflux	65.2	62.4	57.7
Reflux ratio (reflux: product)	4.06	3.04	2.75
Mole fraction alcohol in reflux from condenser B assuming simple condensation	0.835	0.800	0.837
Moles alcohol leaving condenser A in vapor	63.9	62.3	61.1
Moles water leaving condenser A in vapor	12.3	14.8	11.6
Total moles leaving condenser A in vapor	76.2	77.1	72.7
Moles fraction alcohol in vapor from condenser A	0.839	0.808	0.840
Mole fraction alcohol in reflux from condenser A assuming simple condensation.	0.830	0.790	0.833
Moles alcohol leaving column	68.1	67.0	66.2
Moles water leaving column	81.3	83.0	78.8
Mole fraction alcohol in vapor leaving column	0.838	0.807	0.839
Mole fraction alcohol in reflux entering column	0.835	0.803	0.837
Ratio moles feed to moles product	2.54	2.41	2.52
Mole fraction alcohol in feed	0.332	0.338	0.335

It was then possible to calculate values of $\frac{dn}{dx}$ and $\frac{dm}{dx}$ for varying values of x from the above formulas. This has been done for Test 1 as follows, the values of x and y being calculated from the vapor composition curve given by W. K. Lewis.[5] Since no measurement of the alcohol in the waste was given, x_w was assumed to be 0.0001, a value probably somewhere near the fact. The calculated values are plotted in Fig. 2.

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[1] Published as Contribution No. 6 from the Department of Chemical Engineering, M. I. T.

[2] "The Calculation of the Efficiency and the Design of Rectifying Columns," see page 492, this issue.

[3] "La Rectification et les Colonnes Rectificatrices en Distillerie," Paris, 1895, 2nd edition.

[4] "La Distillation Fractionée et la Rectification," Paris, 1917.

[5] "Vapor Composition of Alcohol-Water Mixtures," THIS JOURNAL, 12 (1920), 496.

TEST 1

x	y	$k\frac{dn}{dx}$	$k\frac{dm}{dx}$
0.829	0.838	111	....
0.815	0.828	95	....
0.8	0.815	107	....
0.75	0.783	51	....
0.7	0.753	31	....
0.6	0.703	14.3	....
0.5	0.656	9.0	333
0.45	0.634	7.5	27.8
0.4	0.613	6.3	14.3
0.3	0.581	4.6	6.8
0.2	0.548	3.6	4.5
0.1	0.463	3.7	3.9
0.05	0.575	4.7	4.2
0.03	0.300	7.3	5.0
0.01	0.05	....	35.3
0.003	0.015	....	117
0.001	0.005	....	349
0.0001	0.0005	....	3250

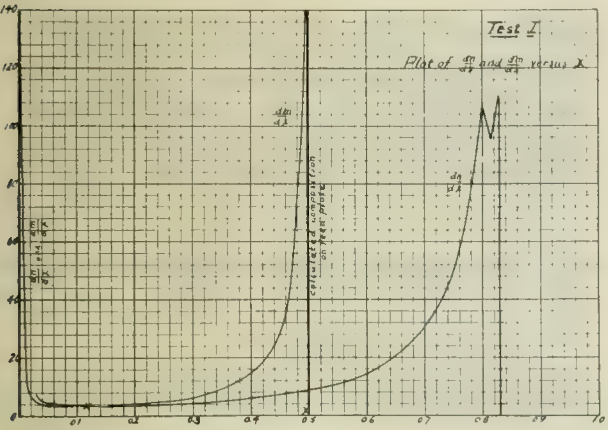

FIG. 2

This plot indicates that the optimum point for introduction of the feed would have been at that point in the column where $x = 0.12$, the number of plates required being a minimum at that point. However, at that point the ratio of the area under the $\frac{dn}{dx}$ curve is to that under the $\frac{dm}{dx}$ as 13.76 is to 3.08, or 4.47, while the ratio of the actual number of plates in the rectifying column to that in the exhausting column was 30 to 16, or 1.88. It is therefore necessary to find by trial that value of x where the ratio of the areas is 1.88. This was found to be at about 0.5 where $\frac{dn}{dx} = 11.88$ and $\frac{dm}{dx} = 6.35$, the total number of plates thus required, if 100 per cent efficient, being 18.23. The average efficiency therefore was

$$\frac{18.23 \times 100}{46} = 40 \text{ per cent.}$$

The plate efficiency for all the tests is:

Test number	1	2	3
Plate efficiency, per cent	40	24	56
Reflux ratio	4.06	3.04	2.75
Composition of distillate	0.842	0.816	0.844

More careful tests on alcohol stills of a similar type by W. A. Peters, Jr.,[6] indicate that the plate efficiency is approximately 70 per cent. He has calculated Test 1 of this paper on the basis of a 70 per cent efficiency and found that the slop should be approximately 0.000002 mole fraction alcohol, instead of the assumed value of 0.0001. Since both of these values of the concentration are so small that they are practically immeasurable, it is evident that a true determination of the plate efficiency cannot be made by merely testing the slop when the alcohol is so nearly completely removed. In order to obtain data on which the efficiency can be calculated, it would be necessary to draw samples from plates higher up in the column on which there was a liquid containing a measurable amount of alcohol. The value of this paper should then lie in its exposition of a method for the calculation of tests on continuous stills.

The wide variations in results thus obtained from the same still operating under not widely varying conditions indicate the desirability of a considerable factor of safety in column design.

NOMENCLATURE

x = Mole fraction of alcohol in the liquid.
y = Mole fraction of alcohol in the vapor.
n = Number of plates above feed.
m = Number of plates below feed.
k = Average plate efficiency.
y_c = Composition of vapor leaving column.
x_w = Composition of waste liquid leaving column.
R_n = Reflux ratio above feed.
R_m = Reflux ration below feed.
R_f = Ratio feed to distillate.
M_L = Molal heat of vaporization in Kal.
Cp = Specific heat.
Kal. = Kilogram calories.

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[6] See first paper in Symposium.

The Simple Distillation of Hydrocarbon Mixtures[1]

By W. K. Lewis and Clark S. Robinson

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IN the laboratory the simple distillation of hydrocarbon mixtures is most nearly represented by the Engler distillation, which consists of the distillation of a known volume of mixture from a simple flask and the recording of the relation between the vapor temperature and the percentage by volume of the original mixture distilled over. When plotted the data give a curve of the type illustrated in Fig. 1 (solid line). This Engler distillation is used universally for the purpose of comparison of petroleums and petroleum distillates, coal tar, light oils, and other complicated hydrocarbon mixtures.

The other extreme from simple distillation is complete fractional distillation which separates a mixture into its several pure components, giving a distillation curve of the type indicated by the broken line in Fig. 1.

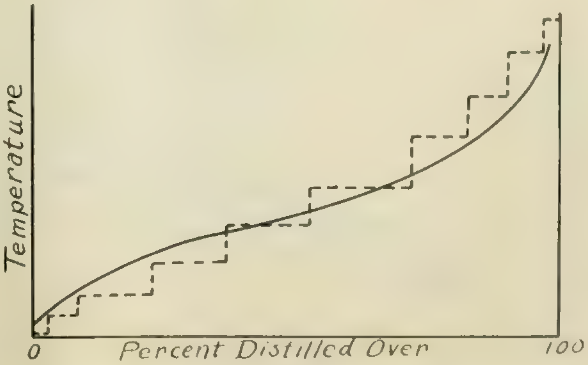

FIG. 1

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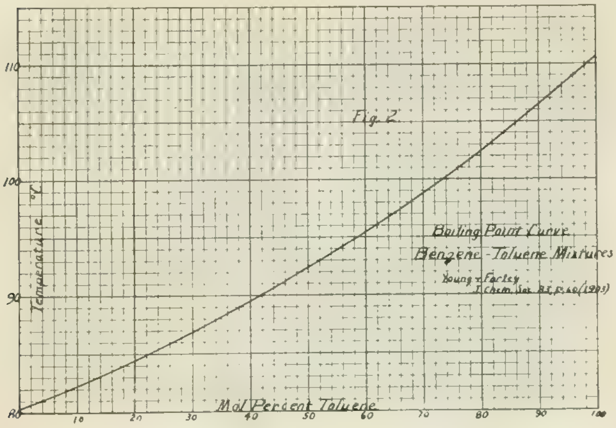
[1] Published as Contribution No. 15 from the Department of Chemical Engineering, M. I. T.

It is possible to predict the Engler distillation curve (first type) if the composition of the mixture be known. It is theoretically but not practically possible to make the reverse prediction, that is, the composition of the mixture, if the Engler distillation curve be known. The simplest case, that of a mixture of two components, will be taken for the purpose of illustration.



The well-known Rayleigh equation for simple distillation is as follows:

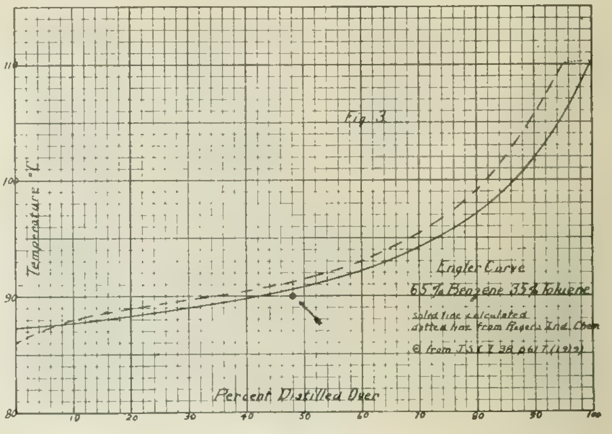
$$\ln \frac{w_2}{w_1} = \int_{x_1}^{x_2} \frac{dx}{y-x} \qquad (1)$$

where w = weight of liquid being distilled,
x = composition of liquid being distilled, and
y = vapor in equilibrium with liquid.

The integration of this equation can be much simplified if Raoult's Law be assumed. Fortunately mixtures of hydrocarbons most frequently met with, such as homologs of the benzene series, or homologs of the methane series, come very close to following this Law. It is probable that any hydrocarbon mixture, the boiling points of the components of which do not differ too greatly, follows it closely enough for practical purposes.

In a binary mixture of two members of the same homologous hydrocarbon series, such as benzene and toluene, whose boiling points are not far apart, the ratio of the vapor pressures at one boiling temperature does not differ greatly from that at the other boiling temperature, and an average value of the ratio may be taken as an approximate constant within this range. Combining this approximation with Raoult's Law, the integrated Rayleigh equation is as follows:

$$\ln \frac{w_2}{w_1} = \frac{1}{\alpha-1}\left(\alpha \ \ln \frac{x_1}{x_2} + \ln \frac{x_2-1}{x_1-1}\right) \qquad (2)$$



where α is the ratio of the vapor pressures of the less volatile and the more volatile components. In this equation, however, w is expressed as moles. The use of this equation is shown in the following example:

One hundred moles of a mixture containing 65 per cent by weight of benzene and 35 per cent of toluene are distilled. This composition corresponds to a mole fraction of 0.686. The ratio of the vapor pressure of toluene to that of benzene at 95° C., half-way between their boiling points, is $\frac{475}{1170} = 0.406$. When the distillation has progressed to such a point that x, the mole fraction of the benzene in the liquid, has dropped from the original value $x_1 = 0.686$ to $x_2 = 0.6$

$$\ln \frac{w_2}{100} = \frac{1}{0.406-1}\left(0.406 \ \ln \frac{0.686}{0.6} + \ln \frac{0.6-1}{0.686-1}\right)$$

when $w_2 = 60.6$.

The weight of benzene present in the residue w_2 will be

$$60.6 \times 0.6 \times 78 = 2830$$

and that of the toluene will be

$$60.6 \times 0.4 \times 92 = 2130$$

Total weight of residue.................... 4960

The total weight of liquid at the start was

$$100 \times 0.686 \times 78 = 5350$$
$$100 \times 0.314 \times 92 = 2890$$
$$8240$$

The per cent by weight distilled over will be

$$\frac{8240-4960}{8240} \times 100 = 39.8$$

The temperature at which a mixture containing 60 per cent mole per cent benzene will boil at one atmosphere can be read from the boiling-point curve shown in Fig. 2, as 89.5° C.,

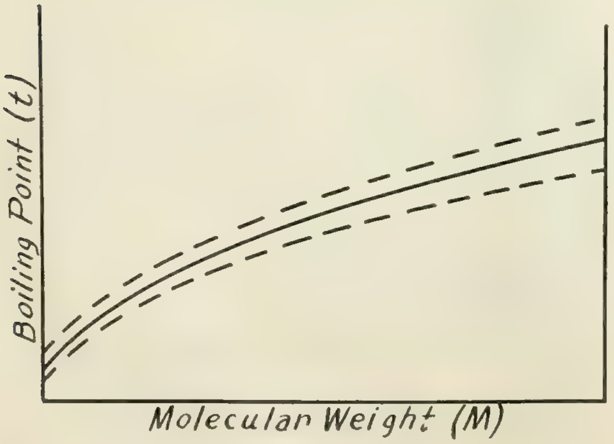


Fig. 4

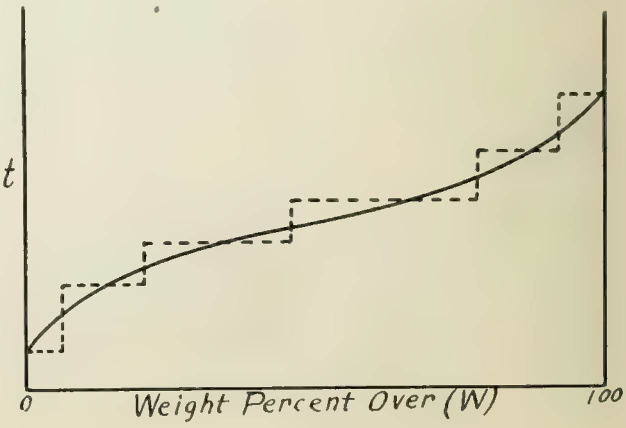


Fig. 5

giving a point on the Engler curve, if the Engler curve be plotted as weight per cent over. These calculations can then be repeated for several values of x_2 as given in Table I. These values, plotted as a curve, are shown by the solid line in Fig. 3.

TABLE I

x_2	w_2	Per cent Over by Weight	Temperature ° C.
0.686	100	...	87.3
0.6	60.6	39.8	89.5
0.5	36.9	61.9	92.4
0.4	23.2	75.7	95.6
0.3	14.75	84.3	98.9
0.2	8.95	90.3	102.4
0.1	4.57	95.0	106.2

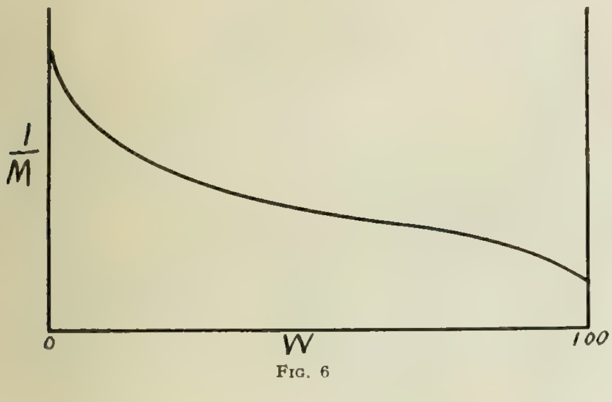


FIG. 6

The dotted line on Fig. 3 is the Engler curve given by F. E. Dodge.[2] This curve was given for volume per cent distilled over, but in the case of benzene-toluene mixtures weight and volume per cents are nearly identical. When compared with the theoretical curve, it shows unmistakable evidence of fractional condensation.

Coleman and Yeoman[3] give a graph for determining the composition of benzene and toluene mixtures. According to them, when a 65 per cent mixture is distilled, the temperature will have reached 90° C. when 48 per cent has been distilled over. This point is indicated on Fig. 3 by an arrow. The variation between the value given by Dodge of 37 per cent and that by Coleman and Yeoman of 48 per cent, and the calculated value of 42.5 per cent, indicates the difficulties which can be expected from partial condensation in the Engler distillation, and emphasizes the care that must be taken to avoid it.

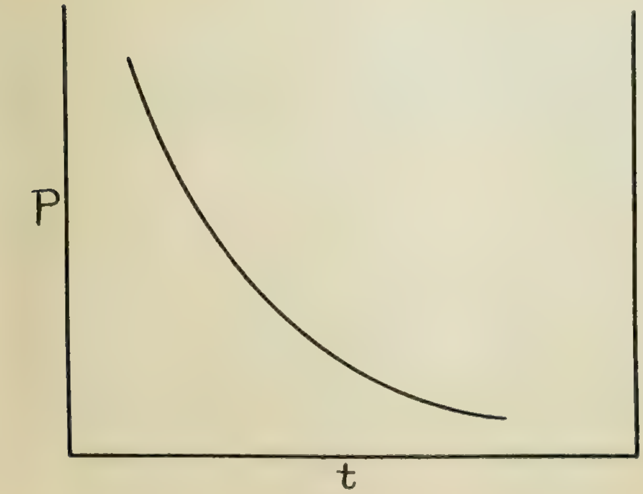


FIG. 8

It is the conviction of the writers that the practice in all Engler distillations should be so modified as to eliminate partial condensation of the vapors. This can be accomplished by providing a chimney around the top of the still so it will be jacketed with flue gases hotter than the vapors. Superheating the vapors cannot change their composition short of cracking, but partial condensation does. The thermometer must be kept wet with liquid by some sort of "percolator." These simple precautions will make the Engler curve reproducible by anyone and independent of rate of distillation. Moreover, the results will then have sound theoretical significance.

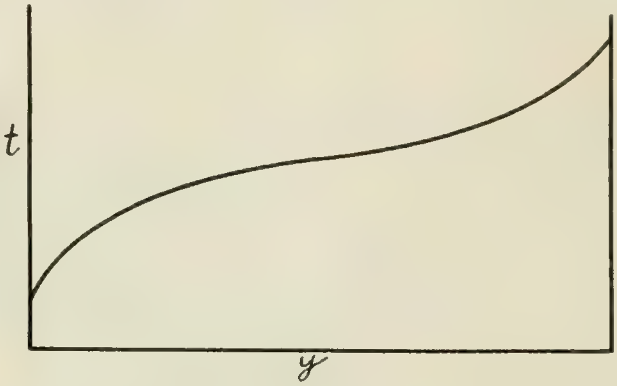


FIG. 7

The method for the prediction of the Engler curve for mixtures of more than two components will now be indicated. As before, it depends upon the assumption of Raoult's Law.

In order to make the method general, assume 100 g. of a mixture with a very large number of components, all belonging to the same homologous hydrocarbon series, as the paraffin series, whose boiling points as function of their molecular weight may be indicated at least approximately by a curve of the type shown in Fig. 4, the actual values lying between the dotted lines, the solid line being an average value. If this mixture be distilled through a fractionating column of sufficient size so that it is separated into its pure components, the resulting fractionation curve would resemble the dotted line in Fig. 5. For a large number of components, this dotted line could be very closely represented by a smooth curve as shown by the solid line.

By combining the curves in Figs. 4 and 5, the curve shown in Fig. 6, plotting 1/M against w is obtained. The area under this curve up to any value of w represents

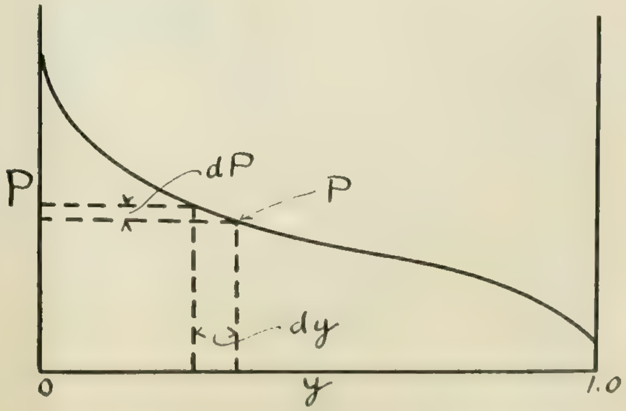


FIG. 9

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[2] Rogers' "Industrial Chemistry," 2nd edition, 490.

[3] *J. Soc. Chem. Ind.*, **38** (1919), 612.

$$\frac{w}{M} = \int_{w_0}^{w_1} \frac{dw}{M}$$

which is the number of gram moles distilled over, based on the original 100-g. sample, the total area being the total number of moles in the original 100 g.

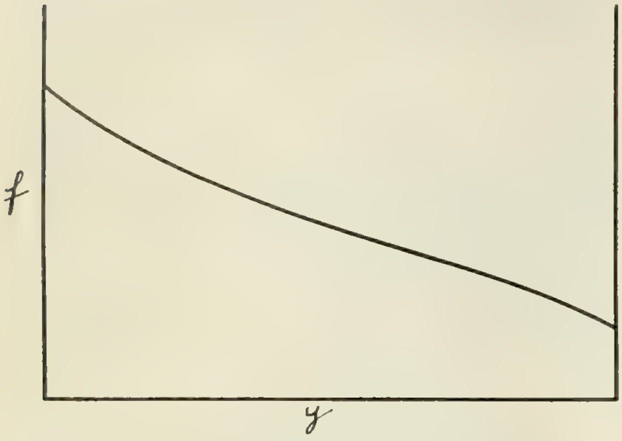


Fig. 10

Indicate the ratio of the number of moles over at any point in the distillation, divided by the total number of moles, by the letter y. Comparing several values of y by means of Figs. 6 and 4, a curve giving the relation between y and t can be constructed as indicated in Fig. 7.

Now construct a curve at some constant temperature of the vapor pressures of the pure components in the mixture at that temperature as a function of the boiling temperatures, t, of these same components at one atmosphere pressure, the result being shown in Fig. 8, where P represents the vapor pressures of the pure components.

Figs. 8 and 7 can be combined as shown in Fig. 9, which is an *isothermal* diagram. Select some pure component, such as that indicated by dy in Fig. 9, which in the pure state exerts the vapor pressure at this constant temperature of P. When in the mixture, however, its partial pressure (by Raoult's Law) will be Pdy. The total pressure exerted by the mixture at the constant temperature chosen will be equal to the sum of all the partial pressures of the components or will be $\int Pdy$, which is the area under the whole curve in Fig. 9.

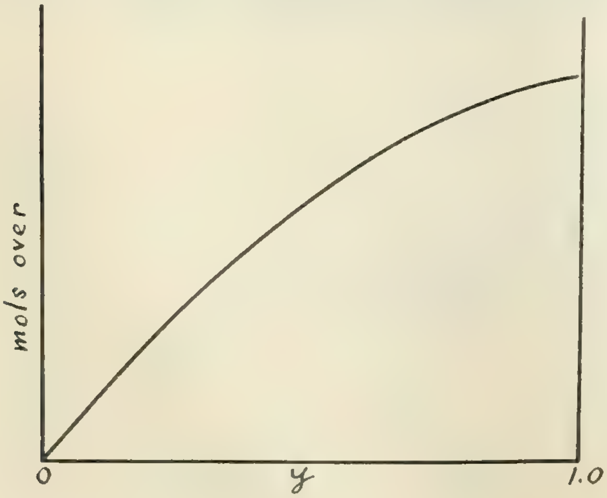


Fig. 11

At the start of a simple distillation at constant temperature, that component, represented by dy, will start to distil over, as will any other component, $d'y$, whose vapor pressure at this temperature will be P′. When a differential amount $d(dy)$ of the first has gone over, an amount $d(d'y)$ will also have volatilized. The ratio of these amounts will equal the ratio of their partial pressures, or

$$\frac{d(dy)}{d(d'y)} = \frac{Pdy}{P'd'y} \tag{3}$$

which when integrated, P and P′ being constants, gives

$$P' \ln \frac{dy}{dy_0} = P \ln \frac{d'y}{d'y_0} \tag{4}$$

If f represents that fraction (molal) of dy that has not come over then

$$P' \ln f = P \ln f' \tag{5}$$

This equation is the generalized form of Equation 2. Since in this equation P and P′ appear as a ratio, the expression is valid over any temperature range in which the ratio remains substantially constant.

Suppose that $d'y$ or f' represents, for instance, the most volatile component in the mixture, it is now possible to calculate the fraction of all the other components which have not gone over when f' has any specific value, for instance, $f' = 0.10$, by substituting the proper values for P and P′ and solving Equation 5 for f. These several values of f (when $f' = 0.10$) can then be plotted as a curve against y, as shown in Fig. 10.

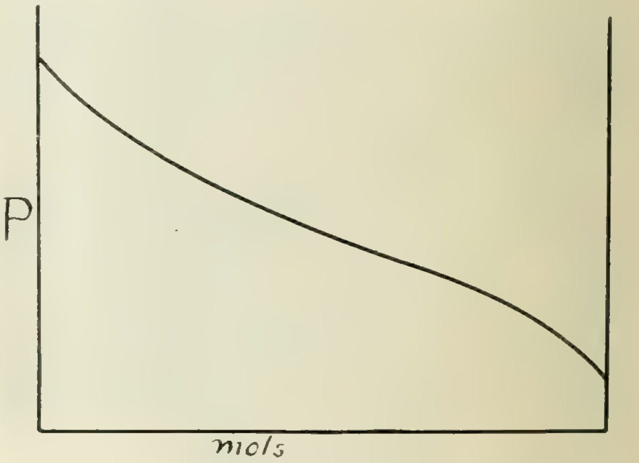


Fig. 12 (for $f' = 0.10$ isothermal)

The area under this curve is the total number of moles of all the components which have not gone over when $f' = 0.10$, and the area up to any value of y represents from Fig. 9 the moles remaining in the shell up to the corresponding value of P.

Construct from Fig. 10, when $f' = 0.10$, a series of areas for the several values of y, and plot as moles up to that value of y (Fig. 11).

Then, combining Figs. 11 and 9, plot moles left in the still up to pressure P divided by total moles left in the still (*i. e.*, mole fraction up to the point P) against the corresponding value of P as shown in Fig. 12. The area under this plot will be the total pressure at this point in the distillation from which can then be calculated the boiling temperature. By repeating this process for other values of f' (for instance, 0.20) a series of points on the Engler curve can be determined.

The Molal Entropy of Vaporization as a Means of Determination of Heats of Vaporization

By **W. K. Lewis** and **H. C. Weber**

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

In 1915, Prof. J. H. Hildebrand[1] pointed out that the molal entropy of vaporization, that is, the latent heat of vaporization of one mole of any liquid divided by the absolute temperature at which vaporization takes place, was nearly identical for all liquids when compared at identical values of vapor concentration. Professor Hildebrand showed data substantiating the claim for the particular concentration of 0.00507 mole per liter.

The authors have found this relationship extremely helpful in estimating the heat of vaporization of liquids, but because one almost never wants the heat of vaporization at this particular concentration, we have found it advantageous to plot what we term the Hildebrand function. In the plots that follow, the ratio of molal heat of vaporization to absolute temperatures at which vaporization takes place has been plotted against the ratio of the pressure at which vaporization takes place (expressed in atmospheres) to the absolute temperature. As a matter of convenience, this latter ratio has been multiplied by 1000.

Range Covered by Data

The data include a list of substances whose boiling points range from that of liquid nitrogen to that of boiling cadmium and zinc. The list includes elements, organic liquids, and inorganic liquids. Even such substances as stannous chloride, ether, and water fall within the range of the curves indicated in the plots.

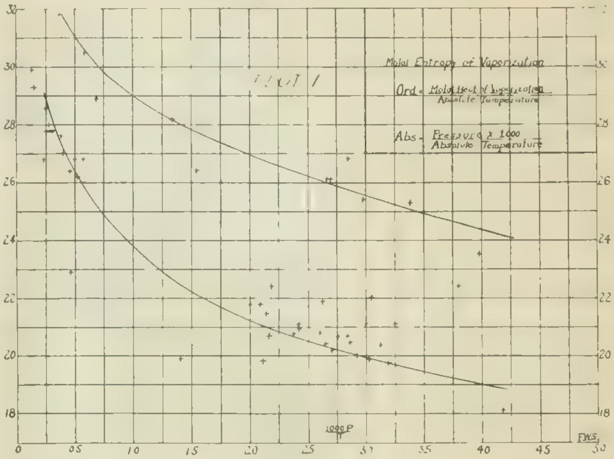
In choosing the data the authors have, however, limited themselves to pressures of about 1 atmosphere or less, but this is no very serious disadvantage because in chemical practice one seldom has need of heats of vaporization at pressures greater than one atmosphere. In the case of water, ammonia, and similar substances in common use, tables are available which give the necessary data at higher pressures. We do feel, however, that the data can be safely extrapolated to pressures somewhat in excess of one atmosphere with a fair degree of accuracy.

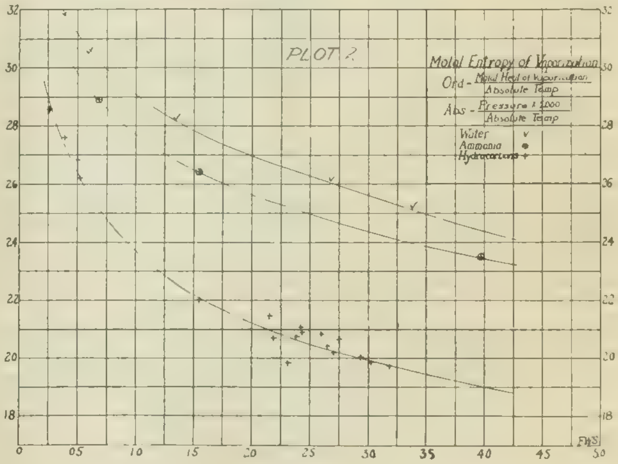
Interpretation of Plots

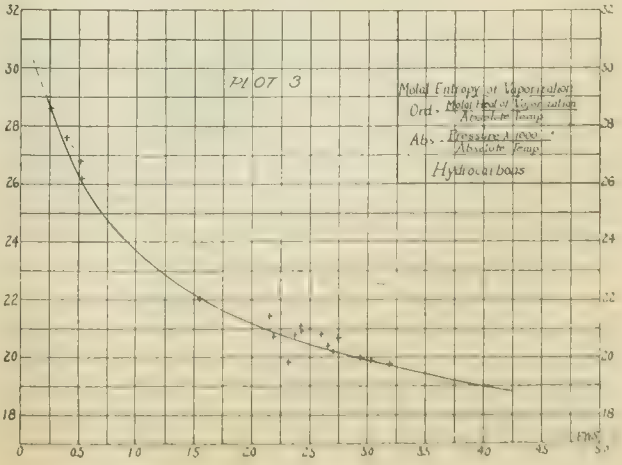
We have indicated on Plot 1 the location of some fifty-odd points.[2] It will be noted that the points fall in a belt about four units wide measured on the vertical scale. It will, of course, be found that a curve drawn through the uppermost points will include data belonging to water, ammonia, alcohol, and other such liquids of an associating or complex nature. A curve drawn through the lowermost points will include all data belonging to the hydrocarbons and nonassociating liquids.

In Plot 2 the writers have drawn three such curves and have indicated by method of plotting to which substances the various points apply. The determination of the heat of vaporization of a substance consists in deciding first of all whether the liquid is likely to be associated. If so, use the upper curve; if not, use the lower curve. Having decided which curve to use, locate on the horizontal margin the value of the ratio P/T (pressure in atmospheres divided by absolute temperature, T). Find by the curve the corresponding value for Q/T on the vertical scale. Multiplying the latter value by T (the absolute temperature) gives the molal heat of vaporization for the unknown substance.

If one is dealing with a given class of compounds, a curve can be drawn for this class which is more definite than if a number of types of compounds are included. Plot 3 shows the data for hydrocarbons, including saturated, unsaturated, and cyclic compounds. It will be noted that no points deviate more than one unit from the full curve drawn among them, *i. e.*, the error in no case exceeds 5 per cent. The dotted curve represents the heat of vaporization *calculated from the vapor pressure curves* of various hydrocarbons by the method of the following article.







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[1] *J. Am. Chem. Soc.*, **37** (1915), 970.

[2] Hildebrand, and Landolt-Börnstein-Meyerhofer "Tabellen," **1912**.

SUMMARY

A variation in Professor Hildebrand's method of plotting molal entropy of vaporization is presented which is considered more useful than the original method. A wide range of data is presented to prove the value of the method, and means of determining heats of vaporization are pointed out.

SUBSTANCE	$t°$ C	L	L/T Abs.	1000 P/T
Nitrogen	−210		21.8	2.0
Bromine	58	7,280	22.0	3.0
Mercury	350	12,400	19.9	1.39
Carbon dioxide	−56	3,790	17.47	2.35
Carbon disulfide	46.2	6,490	20.35	3.13
Carbon tetrachloride	76	7,140	20.45	2.86
Acetone	57	7,270	22.0	3.03
Ether	35	6,500	21.1	3.25
Hexane	68	6,820	20.0	2.93
Pentane	30	6,180	20.4	2.65
Benzene	80	7,300	20.7	2.84
Aniline	183	10,200	22.4	2.19
Nitrobenzene	152	9,740	22.9	0.46
Propylacetate	101	8,200	21.9	2.62
Toluene	111	7,990	20.8	2.60
Ethyl alcohol	78	9,430	26.8	2.85
Chloroform	61.2	7,040	21.1	3.00
Methanol	64.7	8,568	25.4	2.98
Propanol	97.2	9,669	26.1	2.70
Heptane	98	7,500	20.2	2.70
Chlorine	−33.7	4,340	18.1	4.18
Sulfur dioxide	−10.1	6,160	23.4	3.80
Hydrogen sulfide	−61	4,497	21.2	4.73
Ammonia	−34	5,600	23.5	3.98
	−52	....	26.4	1.54
	−66		28.9	0.69
Oxygen	−192	....	21.8	2.09
Chlorine	−73	....	26.8	0.67
Pentane	−13	....	26.2	0.51
Isopentane	−11	....	26.8	0.50
Hexane	+16	....	26.4	0.46
Stannic chloride	55	....	27.0	0.40
Octane	66	....	27.6	0.39
Bromonaphthalene	199	....	28.0	0.28
Mercury	260	....	26.8	0.24
Cadmium	635	....	29.3	0.15
Zinc	757	....	29.9	0.13
Water	50	....	31.8	0.38
	60	....	30.5	0.59
	80	....	28.2	1.33
	100	....	26.1	2.68
	40	....	33.2	0.21
	107	....	25.3	3.38
	24	....	35.3	0.098
Dekane	160	8,600	19.85	2.31
Diisobutyl	90	7,990	22.00	1.55
Diisopropyl	50	6,708	20.76	2.38
Diisopropyl	60	6,562	19.73	3.19
Heptane	90	7,790	21.45	2.14
Hexane	70	6,820	19.89	3.02
Hexylene	0	7,800	28.57	0.253
Octane	120	8,150	20.7	2.16
Cyclohexane	80	7,293	20.65	2.76
m-Xylene	140	8,700	21.05	2.42
p-Xylene	138	8,600	20.94	2.43

Determination of Heats of Vaporization from Vapor Pressure Data[1]

By **W. K. Lewis** and **H. C. Weber**

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

IN the preceding article the authors pointed out a method for estimating heats of vaporization with a considerable degree of accuracy from the Hildebrand function. In this paper attention is called to a method for determining the heat of vaporization of any liquid from its vapor pressure curve, and, *vice versa*, for estimating the vapor pressure curve of a liquid in the neighborhood of one particular point on that curve the data for which are known.

GENERAL DISCUSSION

The vapor pressure curves of all liquids possess great curvature; consequently where only a few points on a curve are known it is very difficult to interpolate either mathematically or graphically with accuracy. On the other hand, the vapor pressure curves of all liquids are more or less parallel, and it is a fact that if instead of plotting the vapor pressure of a liquid at a given temperature one will plot against the temperature, the temperature at which some liquid of reference, *e. g.*, water, exerts the same pressure, one will obtain a curve which is very flat, often sufficiently so to be considered a straight line over quite a wide range of temperature. This fact was first developed by J. Johnston.[2] The method of Johnston is of great value in interpolating vapor pressures where only a few points on the vapor pressure curves are available and can be used for extrapolation over fairly large temperature ranges, for instance, 20° to 50° C., with reasonable accuracy. The probable error in drawing a very flat curve through a number of points is much less than in drawing a curve whose curvature is changing rapidly.

As Johnston pointed out, the above method of plotting can be utilized not merely for interpolation or extrapolation of vapor pressures, but also for the calculation of the heat of vaporization of a liquid from its vapor pressure curve. It is, however, equally possible to use it for the construction of a vapor pressure curve from a single point within a reasonable range from that point.

The method assumes the gas laws to apply to the vapor and hence should not be used in this form at pressures much, if any, above one atmosphere. Below one atmosphere the divergence of vapors from the gas laws is almost always slight.

The Clausius equation applied to the vaporization of a liquid whose vapor follows the gas laws may be written

$$\frac{dp}{pd\mathrm{T}} = \frac{\mathrm{L}}{\mathrm{RT}^2}. \qquad (1)$$

This equation obviously applies also to the liquid of reference

$$\frac{dp_w}{p_w d\mathrm{T}_w} = \frac{\mathrm{L}_w}{\mathrm{RT}_w{}^2}. \qquad (2)$$

The method of plotting t_w against t, given above, is equivalent to placing $p = p_w$, when also $dp = dp_w$.

Dividing Equations 2 and 1 gives, therefore,

$$\frac{d\mathrm{T}_w}{d\mathrm{T}} = \frac{\mathrm{L}}{\mathrm{L}_w}\left(\frac{\mathrm{T}_w}{\mathrm{T}}\right)^2. \qquad (3)$$

The left-hand side of Equation 3 is nothing more than the slope of the $\mathrm{T}_w - \mathrm{T}$ plot mentioned above. Furthermore, when this line is substantially straight this slope may be written $\Delta\mathrm{T}_w/\Delta\mathrm{T}$, *i. e.*, finite temperature differences may be employed in calculation. In any case the determination of the slope of a curve of slight curvature can easily be made with precision.

The following example will serve as an illustration as to how the heat of vaporization may be calculated from vapor pressure data:

At 120° C. the vapor pressure of normal octane is 646.4 mm. The temperature at which water has the same vapor pressure is 95.5° C. At this temperature the heat of vaporization of water is 542.6. Upon plotting a $\mathrm{T}_w - \mathrm{T}$ curve for water and octane, it will be found that the slope is 0.825.

$$\frac{\Delta\mathrm{T}_w}{\Delta\mathrm{T}} = 0.825 = \frac{\mathrm{L}}{(18.02)\ (542.6)} \times \left(\frac{368.5}{393}\right)^2$$

$$\mathrm{L} = 9170$$

$$\frac{\mathrm{L}}{\mathrm{T}} = \frac{9170}{(393)} = 23.3$$

$$\frac{1000p}{\mathrm{T}} = \frac{1000\ (646.4)}{393\ (760)} = 2.16$$

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[1] Combined with preceding paper on Meeting program, as "The Calculation of the Heats of Vaporization of Various Liquids, First, by Means of the Hildebrand Function; Second, from Vapor Pressure Curves."

[2] *Z. physik. Chem.*, **62** (1908), 336, but see also *Phil. Mag.*, **23** [6] (1912), 458; and *Ibid.*, **23** [5] (1886), 33.

The same method may be used for the estimation of vapor pressures from boiling points only. We shall illustrate, however, by a hydrocarbon the vapor pressure curve of which is known, *i. e.*, calculate the vapor pressure of toluene from its boiling point, 110.4° C., in order to be able to compare the result with the experimentally determined vapor pressure.

The equation used to find the heat of vaporization in the previous examples serves here.

$$\frac{\Delta T_w}{\Delta T} = \frac{L}{L_w}\left(\frac{T_w}{T}\right)^2 = \text{Slope of } (T_w - T) \text{ curve.} \qquad (1)$$

The value of L in this equation may be obtained from the preceding article (Plot 3).

$$\frac{1000p}{T} \text{ in this case equals } \frac{1000 \times 1}{383.4} = 2.62$$

The value of $\frac{L}{T}$ corresponding to 2.62 from Plot 3, using the calculated curve, is 22.6, whence,

$$L = 22.6 \times 383.4 = 8650.$$

Substituting this value of L in Equation 1,

$$\frac{\Delta T_w}{\Delta T} = \frac{8650}{18.02 \cdot 542.6} \times \left(\frac{373}{383.4}\right)^2 = 0\ 841$$

$$(100 - t_w) = 0.841\ (110.4 - 90)$$

$$t_w = 82.8°.$$

This means that at 82.8° C. water will have a vapor pressure equal to that of toluene at 90° C. This makes the vapor pressure of toluene 398 mm. at 90° C. Landolt-Börnstein gives a value of 405 mm. for 90°.

If the above calculations are repeated, using for the heat of vaporization of toluene the value given by Landolt-Börnstein, 7990 at 110.4°, we get a value of 420 mm. for the vapor pressure of toluene at 90° C.

It was by calculations the reverse of the above that all the points on the dotted curve of Plot 3 of the preceding article were obtained. In calculating vapor pressures of hydrocarbons one should therefore use the dotted curve of that plot.

While it is true that these equations assume that the gas laws apply to the vapor, if the vapors, both of the unknown liquid and of the liquid of reference, deviate in the same direction and to the same extent from the gas laws, the value of R for the two vapors will be identical and the relationship between the two liquids will be accurately expressed by Equation 3. As a matter of fact, liquids have a tendency to deviate in the same direction from the gas laws, and at low pressures this method of calculation will give results as accurate as much of the experimental data in the literature.

As pointed out by Johnston, it is usually possible to find a liquid of reference which will give a line nearly straight, but it is easier to use water and to measure the actual slope at the point in question because all the properties of water are accurately known and available.

Referring to the plot of the preceding article, it will be noticed that the heats of vaporization of the hydrocarbons as calculated by this method (shown by the dotted curve) deviate from the experimental values when P/T is high. When P/T is low, the agreement is excellent. This is probably due to deviation of hydrocarbon vapors from the gas laws, even below atmospheric pressure.

NOMENCLATURE

L = Molal heat of vaporization.
p = Vapor pressure of the liquid under discussion.
R = The gas constant
T = Absolute temperature in ° K.
t = Temperature in ° C.

SUMMARY

A method of estimating the vapor pressure of a liquid at any temperature, one point on whose vapor pressure curve is known, is presented, and a method of getting heats of vaporization from vapor pressure data by a consideration of the Clausius equation is pointed out.

Present Practice of Dynamite and Chemically Pure Glycerol Distillation

By **J. W. Bodman**

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THE equipment and process used in recent glycerol distillation practice are interesting not only as applied to glycerol distillation but also as representing possibilities in distilling other products, particularly those liquids which show a tendency to decompose partly when distilled directly or alone at normal pressure. As an industrial process eliminating waste and conserving heat energy, modern practice in glycerol distillation is a good example of chemical engineering efficiency.

The principle of operation of glycerol distillation is illustrated in the diagrammatic cut in Fig. 1. By following the vapor piping system, it is plain that the system utilizes the double effect or heat regenerator principle used in multiple effect evaporation. This principle is made use of by injecting into the still, instead of steam, the vapor from evaporating weak glycerol water (called sweetwater) and by superheating this vapor with the hot glycerol vapor from the still.

APPARATUS[1] AND PROCESS

The crude glycerol in the still is heated by means of a continuous closed steam coil, and the vaporized glycerol is distilled over in an atmosphere of superheated water vapor issuing from the perforated spider shown in the illustration. The vapors from the still enter the superheater or heat exchanger where most of the glycerol condenses on the copper tubes. In doing this, there is a transfer of sensible heat as well as latent heat of condensation to the water vapors inside the tubes which are on their way to the spider in the still. The glycerol condensed in the superheater drops into the concentrator. The uncondensed glycerol vapors pass to the cooler or first surface condenser, where the temperature is so regulated with warm water supply that practically all of the remaining glycerol is condensed and removed to the concentrator, while the uncondensed steam vapors, with a small per cent of glycerol vapor, continue on to the final or sweetwater condenser. It will be understood that temperature control of the water in the cooler condenser is regulated so as to allow very little glycerol to enter the final surface condenser. In the final or sweetwater condenser, as it is called, complete condensation of vapors is effected with cold water in the tubes, and the condensate flows by gravity to the evaporator where it is continually being boiled by means of either a closed heating coil or a calandria steam chest designed much after the manner of the usual vertical tube calandria evaporator. The source of heat supply to the calandria or coil in evaporator may be either the exhaust from the still coil or an outside boiler supply. Vapor resulting from the boiling in the evaporator is carried through the superheater or heat exchanger to the still spider, and any

[1] Patented March 9, 1921, Serial No. 450,998, William Garrigue & Co

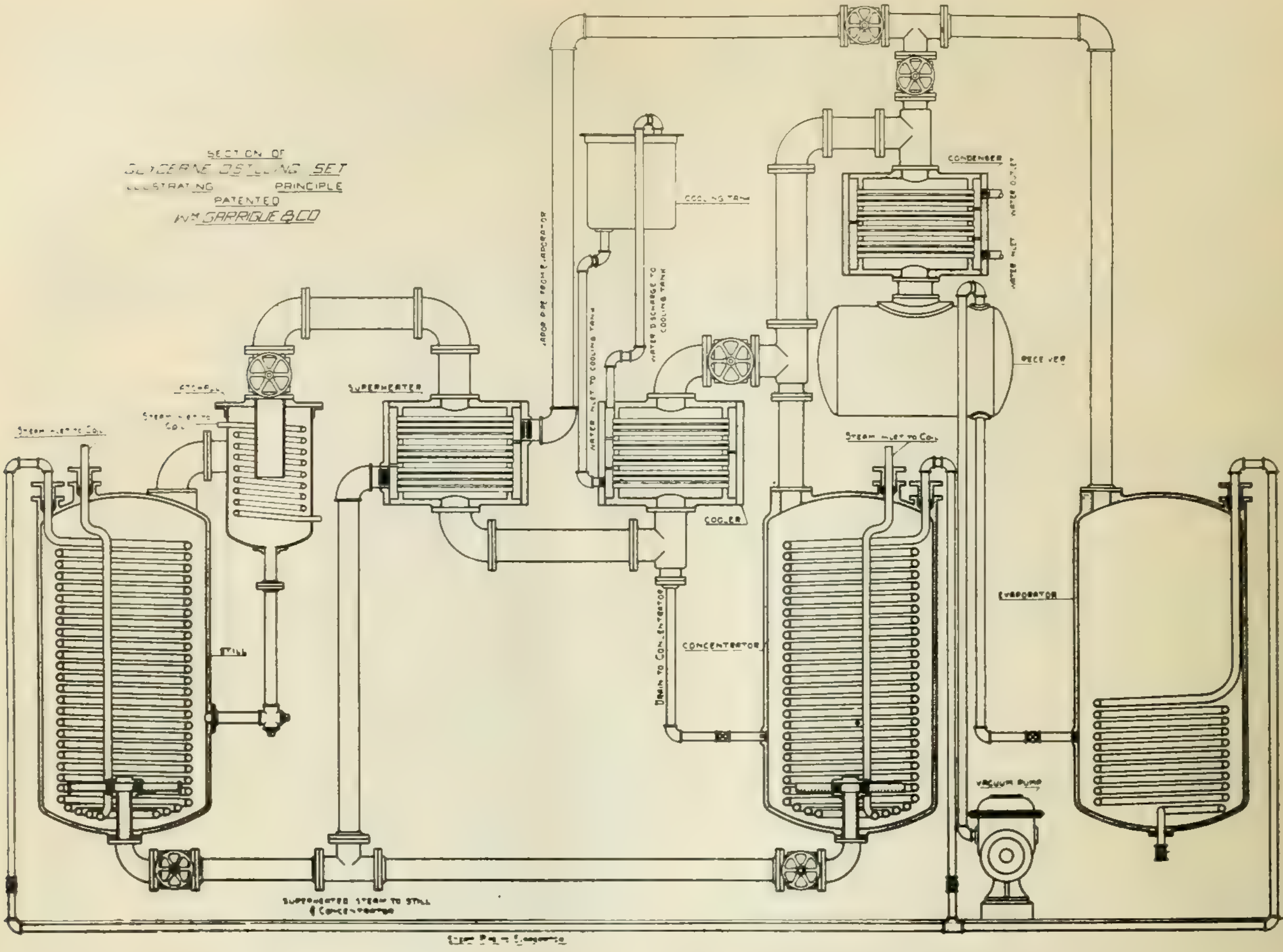

FIG. 1

glycerol carried beyond the cooler is again accumulated in the evaporator.

A constant vacuum is maintained throughout the entire system by a high duty dry vacuum pump connected to the receiver under the final condenser.

The rate of distillation is controlled by a valve supplying steam to the evaporator calandria or coil. The glycerol in the concentrator is maintained or brought up to desired specific gravity by controlling the steam supply to its coil. Water evaporated from the concentrator passes through a vapor outlet to the sweetwater condenser. In practice, the equipment is so constructed that any trimethyleneglycol originally present in the crude glycerol is driven from the concentrated charge by open steam injection. As a rule, however, unless the crude glycerol is unusually low grade, very little impurities will accumulate in the concentrator, but, on the other hand, will be collected in the evaporator. Provision is made for the separation of impurities accumulated in the evaporator by means of usual process of fractionation, the evaporator, condenser, and receiver being operated as a separate unit for this work.

Before placing a plant in operation, the vacuum breakers and other valves on the various units of equipment are closed and the vapor valves opened. The vacuum pump is then started and this is so connected as to draw vacuum on the entire equipment. As soon as the vacuum has reached the desired height, the crude glycerol feed line to the glycerol still is opened and the still filled until 3 or 4 in. of crude glycerol show in the gage glass.

The next step is to feed fresh water to the sweetwater evaporator until 6 or 8 in. show in the gage glass. After this is done, high pressure steam, preferably 150 lbs. gage at the still, is turned into the closed still coil. It is important that this coil be kept free from water so that it will at all times be under steam pressure. It is not difficult to maintain this condition if the valve on the still coil discharge is properly regulated.

Following this, a small amount of steam is turned into the evaporator closed coil or calandria. This is regulated so that the water in the evaporator will begin to boil at the time the crude glycerol reaches the distilling temperature. By this time, the vacuum pump will have reached maximum vacuum obtainable on the distilling system. The vacuum gage should register within 1 in. of the barometer reading.

There is perhaps more danger of priming the still at the beginning of operation than at any other period because if the glycerol is fed into the operating level of 3 or 4 in. showing in the gage glass and closed steam turned on with the vacuum too low, the distillation will start; under these circumstances it is very easy to carry over crude glycerol beyond the catchall, thus contaminating dynamite glycerol in the concentrator.

As pointed out above, when the water in the evaporator begins to boil, the vapors pass through the superheater condenser tubes and are then injected into the crude glycerol in the still through a special spray. In passing through the superheater, vapors from the evaporator are superheated by hot glycerol vapors which surround the superheater tubes. This exchange of heat between the high temperature vapors from the still and the low temperature vapors from the evaporator results in the condensation of glycerol which passes with the flow of uncondensed vapor into the receiver and drops from the receiver into the concentrator.

Uncondensed glycerol vapors which have passed the superheater or heat exchanger, as it may be termed, pass on to the second condenser, which is termed a cooler condenser. The water supply to this second condenser is regulated so that practically all of the glycerol is condensed, but under the vacuum maintained on the system, little of the steam vapors are condensed. The glycerol recovered from the cooler passes to the second receiver and from there flows by gravity to the concentrator. From the second receiver the vapors containing only slight traces of glycerol pass to the final condenser, which is operated cold and condenses all remaining steam and glycerol vapors. This condensate, or sweetwater as it is called in practice, drops into the third receiver from which it flows by gravity to the sweetwater evaporator. From there it is again introduced into the still in the form of superheated water vapor, thus completing the cycle.

In practical operation, the still is given all the injection it will take from the evaporator without causing it to prime or to give a salty distillate. A sample of the liquor passing to the concentrator is taken from time to time and tested for salt.

It is apparent that an increase in the amount of steam to the evaporator coil will cause a fall in the vacuum in the evaporator due to the more rapid generation of steam. The point necessary to watch in this connection is that the vacuum does not fall so low that the sweetwater in the receiver under the final condenser will not flow to the evaporator. The difference in vacuum between the evaporator and the still is limited by the difference in height between the liquor in the sweetwater receiver and the liquor level in the evaporator. An operator readily learns how much he can open the valve on the steam line to evaporator closed coil or calandria so as to secure the proper amount of water vapor injection in the still and at the same time maintain the necessary relative vacuum between the evaporator and the still.

While the above operation is going on, high gravity glycerol liquor is accumulating in the concentrator. When this shows in the lower gage glass of the concentrator, steam is turned into the concentrator closed coil, care being taken at the beginning not to force evaporation, as this might reduce the vacuum on the entire system.

Water evaporated from the concentrator passes through the final condenser and thence into the sweetwater receiver to be returned to the evaporator. After glycerol accumulates in the concentrator and becomes more concentrated, the temperature will rise to about 250° F. This temperature drives most of the water off as rapidly as it runs from the first and second receivers, so that there is no difficulty in finishing to the required specific gravity for dynamite glycerol (1.262 at 15.5° C.) while the still is being cleaned out and prepared for the next run. The concentrator charge is usually considered finished when the temperature rises to 340° F. under full vacuum.

After the plant has been in operation about 0.75 hr., it will be found, if conditions are normal, that the glycerol liquor running to the concentrator will test between 25°–28° Bé., while the sweetwater returning to the evaporator will test less than 1° Bé. Under these conditions, the maximum amount of glycerol is going to the concentrator to be made into dynamite grade.

The still may be fed constantly or intermittently. In any event, care must be taken not to carry too high a liquor level in the still. Three or four inches in the gage glass is considered a good operating level. After the plant is well started, the glycerol level in the still is the only point which requires much attention.

It is general practice to wash the still out once a day. The last feeding to the still should be made so as to allow sufficient time for the still to run down to foots before stopping the distillation to wash out. It requires on the average about 2.5 hrs. time to distil glycerol foots to dryness from an operating level of 3 in. in the gage glass. The actual time required depends upon the quality of the crude, the amount fed to the still, and the degree of dryness desired. If the foots are to be run to the sewer, running down to dryness is an important detail of the operation. An experienced operator soon learns the exact length of time to allow for finishing foots, depending upon the character of material he is handling.

After the foots have been finished properly, steam is shut off from the coils of the still and evaporator, and the vapor valve at the catchall closed. The valve on the line from the sweetwater receiver to the evaporator is also closed. Then the valve on the line from the receivers to the concentrators is closed so as to prevent any liquor which might remain in this line from running to the concentrators and diluting the finished glycerol. This done, the still and the evaporator are completely cut off from the rest of the equipment and the glycerol in the concentrator may be finished, that is, boiled down to the proper specific gravity while the still is being washed out. The vacuum breaker on the sweetwater evaporator is then opened. In doing this, the vacuum on the still is broken through the perforated cross. It is important that the vacuum on the still be broken through the sweetwater evaporator, because if broken by means of the vacuum breaker on the still catchall, the foots are drawn through the injection pipe back into the evaporator and might plug up this line. After the vacuum is completely broken, the vacuum breaker valve on the still catchall is opened and the sweetwater evaporator emptied. This sweetwater may be concentrated to a glycerol which is known as yellow distilled glycerol, or may be returned to dilute glycerol liquors and concentrated with them in a crude glycerol evaporator.

In washing out the glycerol still at the end of a run, only a little water should be run in at first; otherwise, because of the high temperature of the foots and still coil, steam pressure may be generated which would have a tendency to spring the still joints and cause leakage. In order to avoid this, care should be taken that the vacuum breaker on the still is open. As soon as pressure on the still is relieved after introduction of the first wash water, more water is run into the still and steam turned into the coil, leaving the coil drain valve open. The wash water is brought to a boil and the still washed out. In some cases the upper portion of the closed coil in the still is washed out by introducing water from a perforated pipe placed above the coil. If the glycerol foots are to be wasted, the first wash water should be enough to show in the gage glass. This dilutes the foots sufficiently so that the liquor is readily pumped. After boiling for a few minutes, the water is drawn off and the operation repeated until the still is thoroughly cleaned.

If the glycerol foots are to be saved, they are not distilled to complete dryness. Before dropping into the foots tank, several inches of water should be placed in the foots tank, as otherwise the foots will stick to the tank and give trouble in getting into solution.

After the glycerol in the concentrator has been brought up to the proper specific gravity, the concentrator is emptied and the distilling system made ready for the next run.

The finished dynamite glycerol from the concentrator is pumped to the glycerol receiving tank where a small amount of bleach is added. The amount of bleach used varies with character of stock distilled and the color required in the finished product. As a general rule, 1 lb. of bleach per 1000 lbs. of glycerol is used. On a good grade of dynamite glycerol it is only necessary to clarify the finished product. The glycerol, together with the bleach, is circulated from the receiving or bleaching tank through a filter press back into the receiving tank. This operation is continued until the glycerol is sufficiently clear for the desired purpose. The finished glycerol is then run into a drumming tank and either drummed or put in other suitable receptacles ready for shipment.

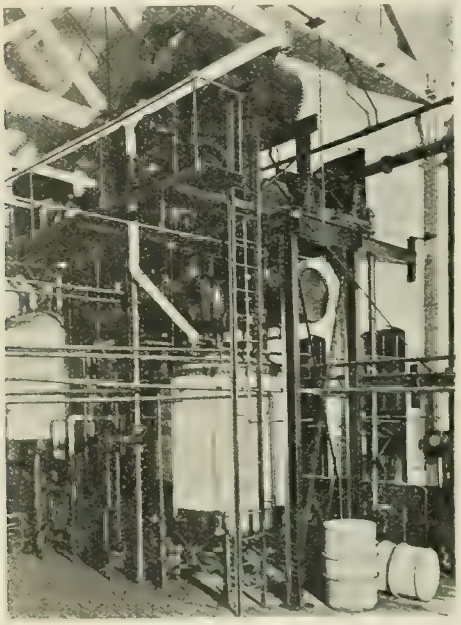

Fig. 2

The above gives us in brief the operating cycle in the production of dynamite glycerol in a typical modern glycerol distillation plant.

C. P. Glycerol

The principle of operation is the same in the production of chemically pure glycerol. For this work a double unit distillation plant is usually installed. An illustration of this plant is given in Fig. 3. One side of this distilling plant operates continuously in the production of dynamite glycerol, while on the other side the dynamite glycerol is redistilled for the production of chemically pure grade. If the crude glycerol as fed to the dynamite still is sufficiently pure, chemically pure grade can be produced by redistillation only. In other cases, it is necessary to give the glycerol liquors an intermediate treatment between the dynamite and C. P. stage. In some cases this treatment consists of diluting, giving a lime treatment with subsequent concentration and redistillation, while in other cases the diluted dynamite glycerol is treated with zinc shavings in the presence of weak hydrochloric acid. Nascent hydrogen produced in this way in the glycerol liquors has a pronounced bleaching effect. Dynamite glycerol after being treated in this manner is again concentrated and redistilled.

There is no measurable loss in the operation of a glycerol distillation plant as described above with steam pressure at 150 lbs. The practical loss depends upon the disposition of the foots. If these foots are treated for the recovery of their glycerol content as crude glycerol and repeatedly returned to the still, there will be obtained a full yield of refined glycerol.

The percentage of glycerol in the foots depends upon the quality of the crude with special reference to the content of total nonvolatile matter. Further, as pointed out above, it depends upon the disposition to be made of the foots how dry it is desirable to distil them. Nonvolatile residue will vary from 10 to about 15 per cent in the crude. The distillation can be carried to a point where this will retain as high as 25 per cent of its weight of glycerol, or if the crude contained 10 per cent of nonvolatile matter and 85 per cent glycerol, there would be 2.5 lbs. pure glycerol remaining in the foots per 100 lbs. of crude, or about 3 per cent of the total glycerol present. With ordinary fair crude glycerol containing 15 per cent residue and 80 per cent glycerol, there would be between 4.5 and 5 per cent of the total glycerol in the foots.

It is considered good practice in distilling all crudes from which the foots can be reworked to give the foots a thorough treatment so that it is not necessary to pay special attention to the percentage of glycerol in the foots. It is easier to clean the still if the distillation is not carried too far, and the capacity of the still is increased. Of course, an exorbitant amount of glycerol is not left in the foots in any case. The aim is to have the residue of 160° C. on the crude carry 40 per cent of its weight of glycerol, in which case the ordinary crude would leave 6 lbs. of glycerol in the foots per 100 lbs. of crude, or between 7 and 8 per cent total glycerol present.

Average practice will obtain 90 per cent of the total glycerol in the crude in the distillate that is ready for boiling down to dynamite glycerol.

The following figures show the distribution of glycerol recovered on a typical dynamite glycerol plant test. These figures are fairly accurate, although not exactly so, as some weights are calculated from measurement. However, they illustrate our purpose:

Sweetwater in evaporator, lbs	1000	
Glycerol by sp. gr., per cent	32.07	
Glycerol, lbs		320.7
Sweetwater in receiver, lbs	1900	
Glycerol by sp. gr., per cent	3.00	
Glycerol, lbs		57.0
Foots, lbs	3600	
Glycerol by analysis, per cent	13.26	
Glycerol, lbs		477.36
Glycerol in concentrator, lbs	17885	
Glycerol by analysis, per cent	99.29	
Glycerol, lbs		17,758
Crude glycerol fed, lbs	23900	
Glycerol by analysis, per cent	79.4	
Glycerol, lbs		18,976
Summary		
Glycerol in crude, lbs		18,976
Glycerol recovered in sweetwater, lbs	378	
Glycerol recovered in foots, lbs	477	
Glycerol in dynamite, lbs	17,758	
Total Recovery	18,613	
Summary of Per cent Yields		
Dynamite glycerol	94.1	
Sweetwater	1.9	
Foots (by difference)	4.0	

The advantages of the distilling system described over older types will be apparent to those familiar with past methods. For the benefit of those not familiar with developments in this field, it may be stated that it was formerly the practice to distil the glycerol, using expanded and reheated steam. The source of supply for the open injected steam was a boiler outside of the glycerol distilling system, so that there was a continuous accumulation of sweetwater which had to be re-evaporated in order to recover its glycerol content. The vapors resulting from this evaporation were not utilized in distilling glycerol but were condensed and run to the sewer. It will thus be seen that the amount of sweetwater which was concentrated under the older systems was much greater than is now required, in fact, the amount of sweetwater concentrated in a modern plant consists only of the fresh water charged to the sweetwater evaporator when starting up the plant plus the water present in the original crude glycerol.

The saving which is thus effected is clear from the following figures:

Assuming 2 lbs. of injected open steam in the still per lb. of dynamite glycerol produced, a plant producing 800 lbs. of glycerol per hr. would inject 11,420,000 lbs. of steam per year, or 38,000 lbs. of steam would be injected in the still per working day. On a yearly basis, this amounts to 335,000 b. h. p. At a rate of 2 cents per b. h. p., the cost of evaporating the sweetwater obtained in one year's operation would amount to $6700. As all of the steam openly injected in the still must be transferred and finally evaporated to sweetwater crude which is again distilled, the amount of $6700 represents the saving of a modern plant compared with older types, considering only the feature of sweetwater evaporation.

The controlling of glycerol passing to the sweetwater condenser by means of water-cooled condensers in place of air condensers and the including of evaporator and concentrator equipment as part of the glycerol distilling set under the same vacuum system rather than operating them as separate units, represents another essential difference between modern and old type plants. Present practice permits the recovery of more than 90 per cent of the glycerol in the crude in the form of dynamite, against about 75 per cent in former methods, or about 20 per cent more glycerol is obtained in the form of dynamite grade by means of modern equipment. On a plant of 800 lbs. per hr. capacity, this amounts to an additional saving of $11,520 per year, assuming the refining cost at only 1 cent per pound.

SUMMARY

Modern glycerol distillation equipment:

1—Enables marked economies in steam and power consumption.

2—Gives highest glycerol yields by eliminating loss of glycerol through handling and evaporating large quantities of sweetwater.

3—Gives maximum recovery of glycerol in the form of high gravity dynamite or C. P. glycerol in a single distillation.

4—Greatly economizes floor space, by including the evaporator and concentrator units as part of the distillation system and under the same vacuum system.

Wood Turpentine

[ABSTRACT]

By C. A. Lambert

HERCULES POWDER CO., HATTIESBURG, MISSISSIPPI

WOOD turpentine is made from stumps, down wood, and sawmill slabs, by destructive distillation or by steam distillation, while spirits of turpentine is the volatile part of the oleoresin exudate from the scarified living tree.

In the manufacture of steam distilled turpentine, 14-ton lots of finely shredded material are distilled with steam at approximately atmospheric pressure. The average recovery from each charge is 112 gal. of crude turpentine, or 8 gal. per ton of wood.

The physical characteristics of the crude product are:

Specific gravity, 15° C.	0.877
Distillation range:	
5 per cent over at 162° C.	
48 per cent over at 170° C.	
95 per cent over at 212° C.	
Unpolymerized, per cent	0.8

The crude turpentine consists largely of α-pinene, dipentene, and α-terpineol. There have also been isolated β-pinene, camphene, *d*- and *l*-limonene, cineol, fenchyl alcohol, and other terpene derivatives and hydrocarbons.

Spirits of turpentine is largely a mixture of α- and β-pinene, and the problem of the wood turpentine manufacturer is to distil his crude oil in such a way as to secure a product as nearly as possible like the best grade of spirits. Technical control has improved the product to a point where practical tests cannot distinguish the distilled product from the spirits.

The crude product is distilled over soda-ash from a refining still provided with a Hempel or Barbet plate column. About 60 per cent of the crude turpentine is made into so-called pure wood turpentine and 40 per cent into pine oil.

The physical properties of the pure wood turpentine are as follows:

Specific gravity, 15° C	0.863
Refractive index, 20° C	1.468
Unpolymerizable, per cent	1.4
Refractive index, residue, 20° C.	1.490
Initial boiling point, ° C	153
Distillation range:	
91 per cent below 170° C.	
Color	Standard or better
Acidity	Trace
Water	Trace

A large sample of pure wood turpentine distilled through a Hempel column gives the following fractions:

	Identified as:
Approximately 2 per cent below 150° C.	
Approximately 70 per cent below 160° C.	α-Pinene
Approximately 3 per cent below 168° C.	β-Pinene
Approximately 15 per cent below 190° C.	Dipentene and terpinene
Approximately 7 per cent below 350° C.	Terpineol, heavier terpene derivatives and polymers

From the heavy ends of the crude turpentine, steam distilled pine oil is obtained by fractionation. It is a mixture of dipentene, terpineol, and other terpene derivatives, with the following physical properties:

Specific gravity, 15° C.	0.930 to 0.938
Unpolymerizable, per cent	3 to 3.5
Refractive index, 20° C.	1.479
Color	Very light straw
Odor	Pine oil
Water, maximum per cent	1.6

Boiling range:

Per cent	° C.
5	189
10	198
20	204
30	206
40	208
50	210
60	212
70	213
80	214
90	217
95	222

Physical characteristics can be varied considerably to meet demands for flotation oils, paints, disinfectants, and pharmaceuticals.

Benzene Purification

[ABSTRACT]

By S. S. Heide

1922 AVE. G, ENSLEY, ALABAMA

CRUDE light oil is recovered from by-product coke oven gas by absorption in paraffin oil. It varies in color from light straw to dark amber, according to its contamination with the wash oil used in its recovery. Its composition is as follows:

	Per cent
Finished fore runnings	1.00
C. P. benzene	62.00
C. P. toluene	15.00
Refined light solvent	3.00
Crude heavy solvent	4.50
Naphthalene	2.50
Finishing still residue	4.00
Wash oil	5.00
Acid washing loss	3.00

The first step in the purification of benzene is distillation of the crude light oil in a column with indirect steam. The cuts are as follows:

	Per cent of Light Oil Used	Distillation
90 per cent crude benzene	70.0	90 per cent 100° C.
90 per cent crude toluene	13.5	90 per cent 120° C.
Crude light solvent	4.5	F. D. 130° C. 90 per cent 160° C.
Crude heavy solvent	4.5	F. D. 160° C. 90 per cent 200° C.
Residue:		
Naphthalene	2.5	
Wash oil	5.0	
TOTAL	100	

The crude heavy solvent may be used directly as a fuel oil or as a solvent in mixing pitch paints. By polymerization large yields of resin may be obtained from this fraction. Naphthalene is separated from the naphthalene-wash oil residue by crystallization, and the wash oil is returned to the scrubbing system.

The crude distillation fractions are separately washed with sulfuric acid in lead-lined agitators. The benzene fraction is rather difficult to wash down to a proper color test, on account of the nature of the acid sludge produced in the washing. A clean separation is obtained in the toluene fraction. The light solvent fraction heats up violently and produces a very viscous and easily emulsified product.

After a water wash, the acid-washed product is neutralized with caustic soda, soda-ash or milk of lime, and is then fractionated in a column still if a C. P. product is desired. The cuts are:

Finished fore runnings	C. P. toluene
C. P. benzene	Rerun toluene
Rerun benzene	Refined light solvent

The residue in the still is a resinous material, somewhat similar to the polymerized coumarone and indene compounds found in the crude heavy solvent. This material is disposed of as a fuel, preferably mixed with crude heavy solvent or tar. The refined light solvent is essentially a mixture of the three xylenes. These are separated by sulfonation to remove the meta compound, followed by fractional distillation of the *p*- and *o*-xylenes.

The writer has recently observed the manufacture of C. P. benzene in which the crude motor benzene fraction, containing all the benzene, toluene, and light solvent present in the original light oil, was washed and distilled for C. P. benzene. The products gave better color tests than were obtained by washing and distilling the 90 per cent crude benzene fraction, less acid was required, a better separation was obtained in the agitator, and very good yields of C. P. benzene were obtained.

The Efficiency and Design of Rectifying Columns for Binary Mixtures[1,2]

By W. K. Lewis

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

Basic equations of general applicability have been derived, by means of which it is possible to calculate the theoretical rate of rectification within any column from the terminal conditions and the amount of overflow, and compare this rate with that actually realized. The results of these calculations have been found to agree satisfactorily with actual tests. A complete example has been computed showing the use of these equations in the design of a continuous column, the determination of minimum overflow, of the best practical overflow, of the number of plates required and of the point of introduction of the feed.

A FRACTIONATING column is an apparatus designed to enrich the volatile components in the vapors arising from a still by allowing these vapors to interact with condensate produced by the partial condensation of the vapors previously given off by the same still. The most familiar type of column employs a succession of plates covered with liquid through which the vapor bubbles. The mathematical theory of such a column as applied to the distillation of binary mixtures was first developed by Ernest Sorel,[3] who calculated the enrichment from plate to plate by equating the amount of energy and of matter entering and leaving each plate and by assuming that equilibrium was realized between the vapors and the liquid through which they bubbled. Sorel applied his method successively from one plate to the next in a column. In consequence the computations become very involved and it is difficult to visualize what is taking place. The following is merely a modification of Sorel's method, which simplifies computation and makes it possible to present results in graphical form.

The derivation will assume a column in continuous operation, with the feed, *i. e.*, the binary mixture to be separated, entering the middle of the column. The results may, however, be applied to a discontinuous column at any particular instant during its operation, provided the amount of condensate in the column is small in proportion to the amount in the still.

Constant Molal Overflow

Where a column is large so that its surface area is small compared with the amount of vapor rising through it or where a small column is properly lagged, heat loss from the sides by radiation and conduction is negligible in comparison with the heat quantities carried by the vapor up through the column. As the vapor rises through the column and part of it condenses upon a given plate, an equivalent amount of liquid must be vaporized from that plate so that its heat of vaporization will equal that of the condensed vapor.

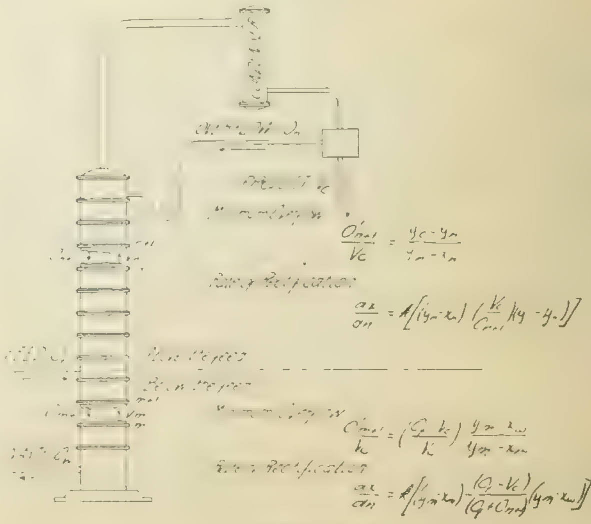

Fig. 1

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[1] Received April 11, 1922.

[2] Published as Contribution No. 16 from the Department of Chemical Engineering, M. I. T.

[3] "La Rectification de l'alcohol," Paris, 1893.

Liquids can be divided into two groups, the associating and nonassociating liquids. Within each group the molal heat of vaporization divided by the absolute temperature is substantially constant, provided the boiling temperatures are not far distant from each other (Trouton's rule). Since distillation is a serious problem only where the boiling points of the components are nearly the same, this is equivalent to saying that the molal heats of vaporization of components in the column will be practically equal if both components are associating (water, ammonia, alcohol, etc.) or if both are nonassociating (hydrocarbons and most organic liquids). Let us assume temporarily that the two liquids in the column belong to the same group; hence their molal heats of vaporization are nearly the same. On the basis of this assumption, for each mole of high boiling constituent condensed out of the vapor a mole of low boiling constituent must be volatilized from the liquid, or in other words, above or below the feed plate, both the molal overflow from plate to plate and the moles of vapor passing up the column must be constant or nearly so throughout the column. The moles of vapor will, however, obviously be greater below the feed plate than above if the feed enters below its boiling point, since some vapor must condense to heat it up. In all cases the overflow is greater below the feed plate than above it, as a result of the amount of mixture fed into the column.

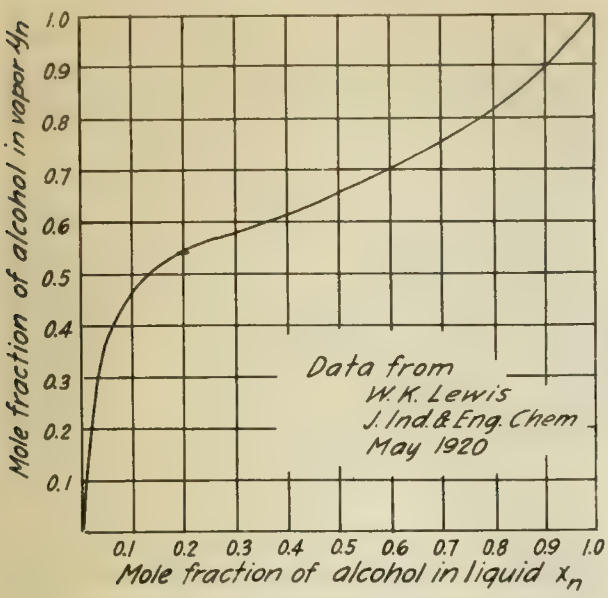

FIG. 2—VAPOR COMPOSITION CURVE FOR ALCOHOL AND WATER

NOMENCLATURE

The nomenclature is indicated by Fig. 1. In this figure there is shown for sake of simplicity a single condenser, so that the overflow back into the column is of the same composition as the product. However, this has nothing to do with the derivation and does not affect the validity of the formulas.

Let each plate be designated by a number. Start numbering the plates from the feed plate upward and downward, the plate on which the feed enters being the zero plate. Call any particular (variable) plate above the feed plate the n^{th} plate and below it the m^{th}. Call the top plate the p plate and the still, or, if none, the bottom plate, the w plate. Call the amount of vapor, measured in moles per unit time, passing any particular section, V, and the amount of liquid for overflow passing the section O. These quantities are to include the moles of both components in the vapor and overflow. Designate the point of origin of the particular vapor or overflow referred to by the use of a subscript: thus, V_n is the moles of vapor rising from the n^{th} plate, while O_{n+1} is the moles of overflow coming down to that plate from the plate above. Use the subscripts f and c to refer to the feed line and to the condenser, respectively. Thus O_f is the amount of feed and V_c is the amount of product. Call the mole fraction of the more volatile component in the liquid x and the mole fraction in the vapor y. Again indicate the liquid to which reference is made by subscripts, thus x_w is the mole fraction of volatile component in the waste or slop leaving the still at the bottom of the column, while y_m is the mole fraction of the same component in the vapor arising from the m^{th} plate. The quantities required in discussion are assembled in the following table:

x = Mole fraction of more volatile component in liquid.
y = Mole fraction of more volatile component in vapor.
V_c = Moles of distillate produced per unit time.
y_c = Mole fraction of more volatile component in the distillate produced
O_{n+1} = Moles of overflow from plate $n+1$ to plate n.
x_{n+1} = Mole fraction of more volatile component in overflow O_{n+1}.
V_n = Moles of vapor passing from plate n to plate $n+1$ per unit time (both components included).
y_n = Mole fraction of more volatile component in vapor V_n.
O_f = Moles of the mixture fed to the column per unit time (both components included).
x_f = Mole fraction of more volatile component in feed, O_f.
O_w = Moles of waste per unit time.
x_w = Mole fraction of more volatile component in waste O_w.
O'_{n+1} = Theoretically minimum overflow from plate $n+1$, per unit time.
$\frac{dn}{dx}$ = Rate of increase in concentration of liquid per plate.
k = Fractionation efficiency of the tower and plates, *i. e.*, ratio of theoretically required to actual requirement.
n = The number of the plate under consideration, counting from the feed plate up.
m = The number of the plate under consideration, counting from the feed plate down.
Q_n = Heat of vaporization of V_n (molal).
r_1 = Heat of vaporization of more volatile component (molal).
r_2 = Heat of vaporization of less volatile component (molal).

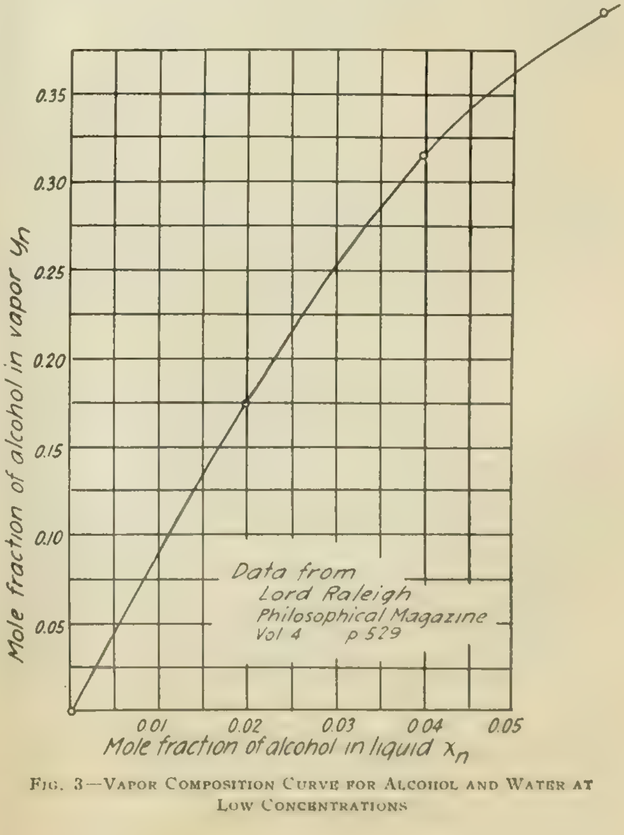

FIG. 3—VAPOR COMPOSITION CURVE FOR ALCOHOL AND WATER AT LOW CONCENTRATIONS

While the reasoning employed and the equations developed are general, it is easier to visualize each step and appreciate its significance by discussion of a special case. Consequently the following will refer to the case treated by Sorel, the separation of alcohol and water, alcohol being the more volatile component.

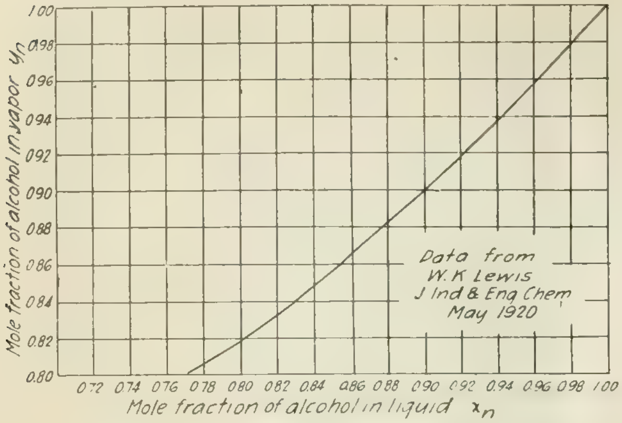

FIG. 4—VAPOR COMPOSITION CURVE FOR ALCOHOL AND WATER AT HIGH CONCENTRATIONS

BASIC EQUATIONS

Consider the whole apparatus above a section drawn between the n^{th} and the $(n+1)^{th}$ plate just below the latter. The only thing entering this section is the vapor from the n^{th} plate, V_n. Leaving it is the product V_c, and the overflow from the $(n+1)^{th}$ plate, O_{n+1}. Therefore

$$V_n = O_{n+1} + V_c$$

Furthermore the total alcohol entering this section must equal that leaving it, *i. e.*,

$$y_n V_n = x_{n+1} O_{n+1} + y_c V_c.$$

Whence,

$$O_{n+1}/V_c = \frac{y_c - y_n}{y_n - x_{n+1}} \qquad (1)$$

and

$$x_{n+1} - x_n = y_n - x_n - \frac{V_c}{O_{n+1}}(y_c - y_n) \qquad (2)$$

This quantity, $x_{n+1} - x_n$, is the enrichment per plate, *i. e.*, from one plate to the plate above it. Since this enrichment is usually small, it is substantially identical with the slope of the curve obtained by plotting composition, x, against number of plates, n, *i. e.*, it equals dx/dn. Hence

$$dx/dn = y_n - x_n - \frac{V_c}{O_{n+1}}(y_c - y_n) \qquad (3)$$

Since these equations represent nothing but equality of input and output, their *validity* cannot be questioned. Their *utility*, however, is limited by the uncertainty as to the relation between x_n and y_n actually existing in a column. If we assume *perfect rectification*, *i. e.*, that equilibrium is realized between the liquid on a plate and the vapor rising through it, these equations are valid and can be used to calculate the theoretically minimum number of plates required for a given rectification, by combining them with the experimentally determined relation between x and y for the mixture under consideration. Calling Δn the number of plates necessary with perfect rectification to enrich from x_1 to x_2, integration gives

$$\Delta n = \int_{x_1}^{x_2} \frac{dx}{y_n - x_n - V_c(y_c - y_n)/O_{n+1}} \qquad (3a)$$

which may be evaluated graphically.

For conditions of perfect rectification below the feed plate, one can derive similarly

$$\Delta m = \int_{x_1}^{x_2} \frac{dx}{y_m - x_m - (O_f - V_c)(y_m - x_w)/(O_f + O_{n+1})} \qquad (4)$$

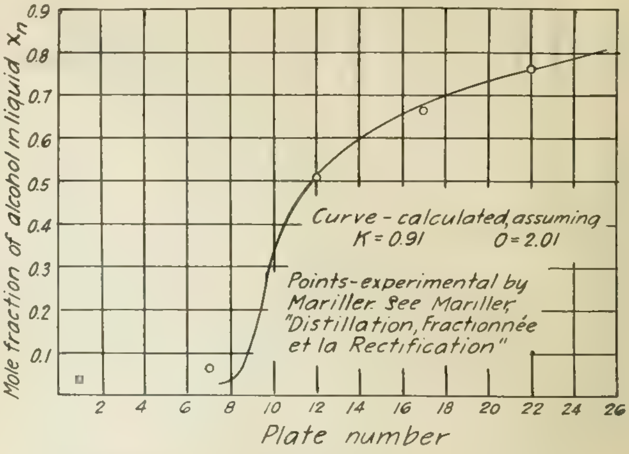

FIG. 5—AGREEMENT BETWEEN CALCULATED AND ACTUAL RESULTS IN DISTILLATION

In using these equations, it must be kept in mind that, even in an indefinitely tall column the rate of rectification, dx/dn, must be positive and cannot possibly be less than zero; whence inspection of Equation 3 shows that the ratio of reflux to distillate cannot fall below the theoretically minimum value

$$O'_{n+1}/V_c \geq (y_c - y_n)/(y_n - x_n) \qquad (5)$$

Similarly below the feed plate,

$$O'_{m+1}/(O_f - V_c) > (y_m - x_w)/(y_m - x_m) \qquad (6)$$

Indeed the overflow at each point in the equipment must be kept distinctly larger than these limiting minimum values in order to have rectification go on in the column at a reasonable rate.

Inspection of Equation 3*a* shows that the integral may easily be evaluated in the case already referred to, where the molal overflow O_{m+1} is constant from plate to plate. This is substantially the case for alcohol-water mixtures and for all mixtures of hydrocarbons whose boiling points are close together (*e. g.*, benzene-toluene, etc.). This simplification makes it much easier to visualize what is happening

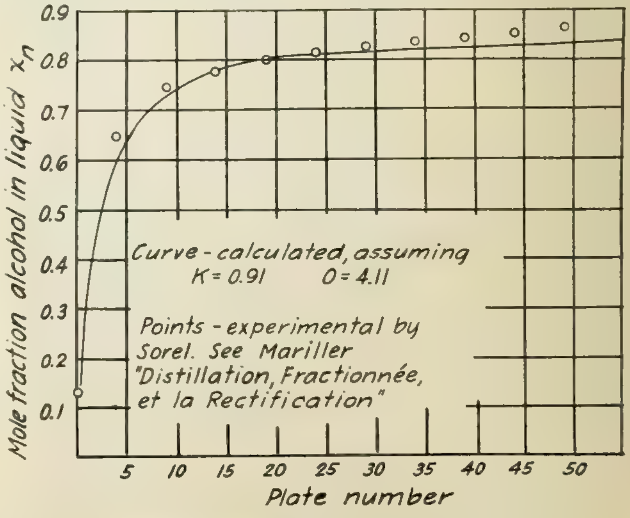

FIG. 6—AGREEMENT BETWEEN CALCULATED AND ACTUAL RESULTS IN DISTILLATION

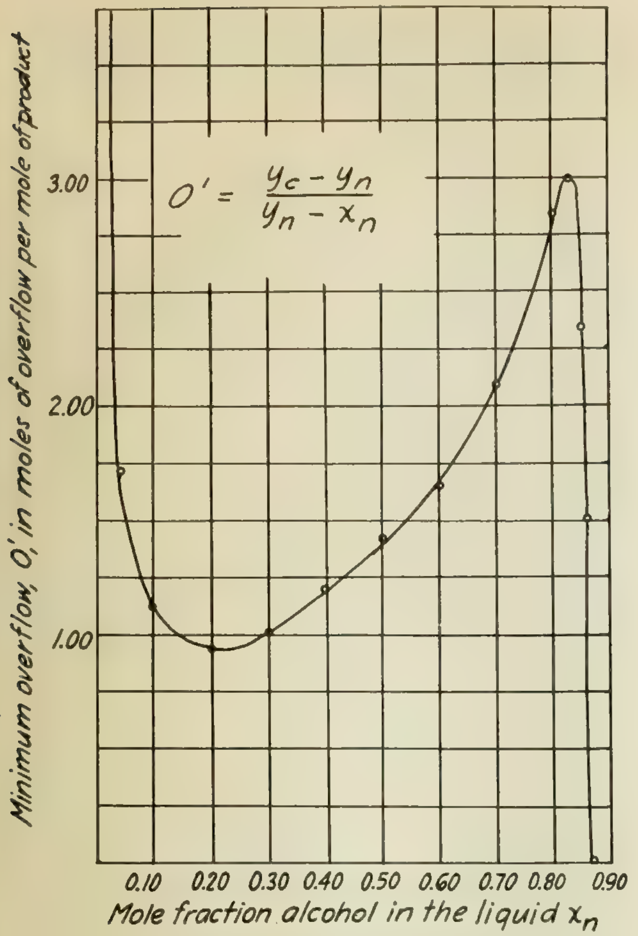

FIG. 7—MINIMUM OVERFLOW ABOVE FEED

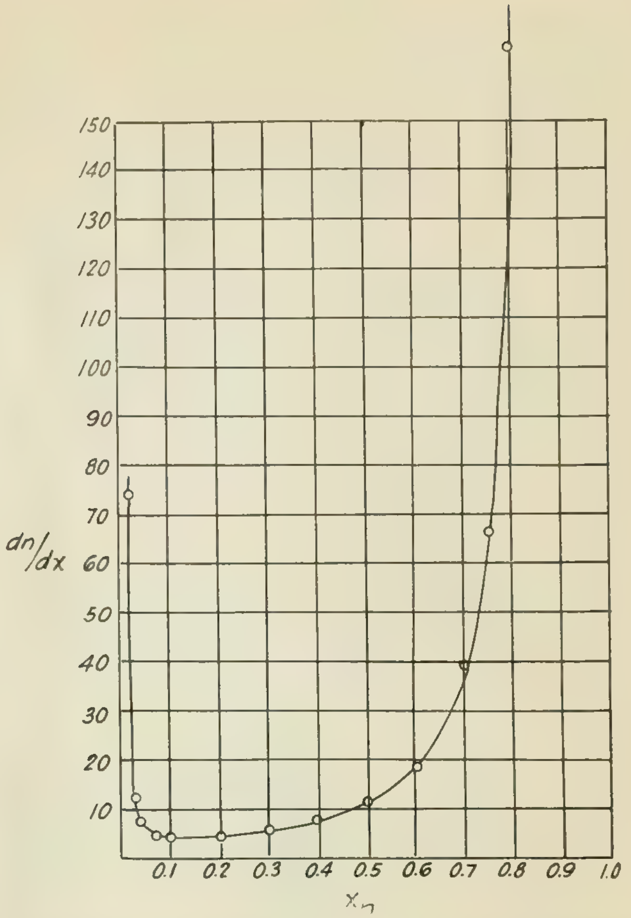

FIG. 8 dn/dx vs x_n ABOVE THE FEED PLATE. PROBLEM O = 5.0 MOLES

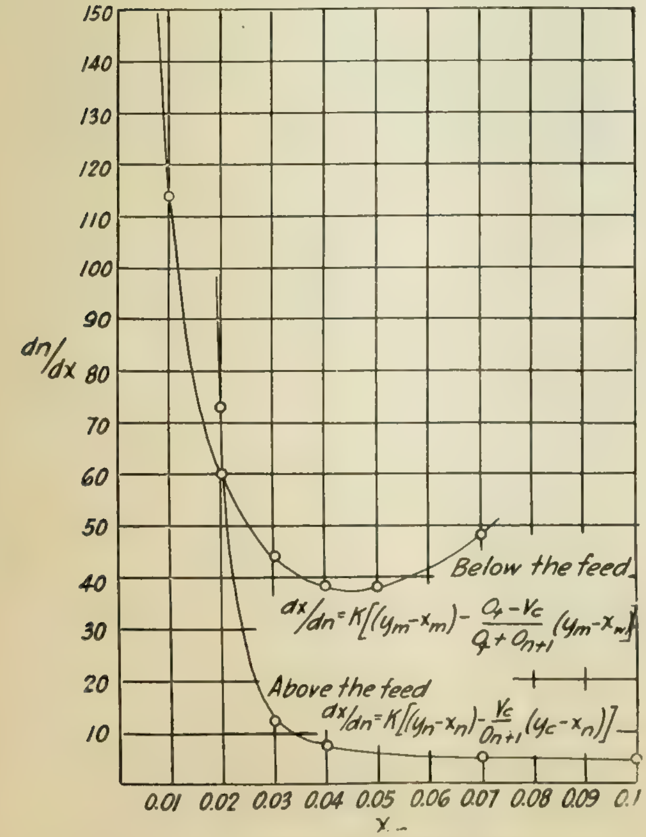

FIG. 9—dn/dx vs. x_n AT FEED PLATE. PROBLEM O = 5.0 MOLES

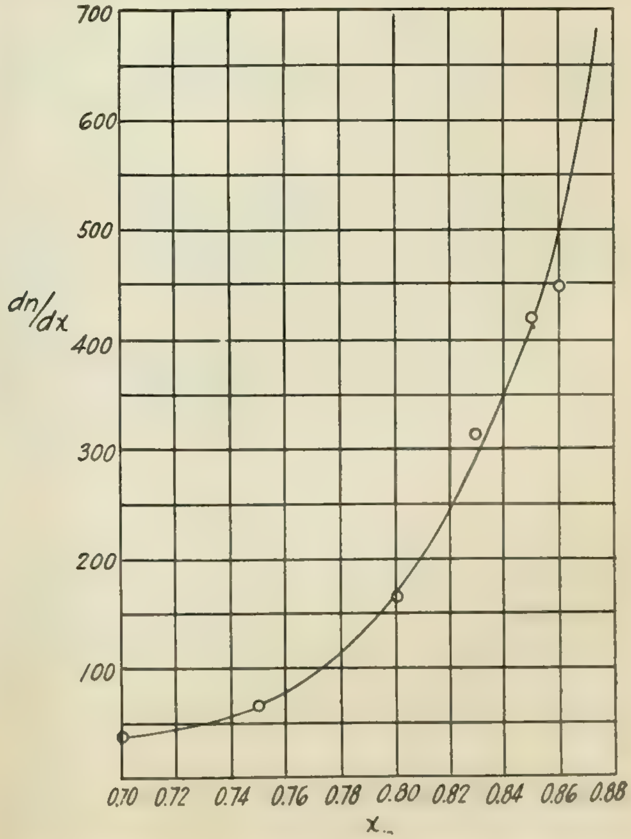

FIG. 10—dn/dx vs. x_n AT TOP OF COLUMN. PROBLEM O = 5.0 MOLES

in the column and is therefore adopted in the following paragraphs.

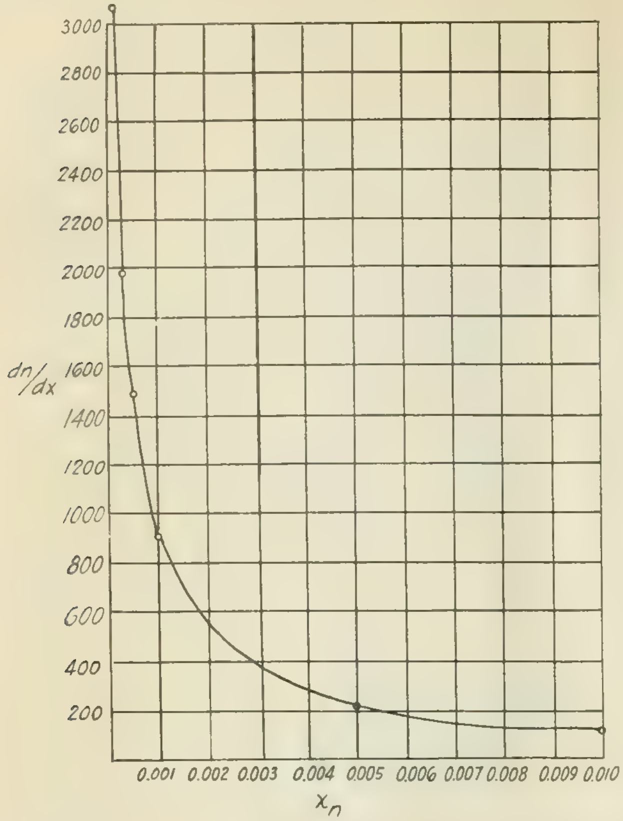

FIG. 11—dn/dx vs. x_n BELOW THE FEED PLATE. PROBLEM O = 5.0 MOLES

Quantitative discussion will be limited to alcohol-water mixtures, and plots of vapor composition, y, as a function of liquid composition, x, are given in Figs. 2, 3, and 4. The two last give the data at the two extremes of the curve.

TEST RESULTS

No adequate data are available in the literature to test out properly these methods of computation. Mariller[4] quotes results of tests on alcohol-water mixtures by Sorel and himself, but does not give overflow. By estimating both overflows and plate efficiencies from the data he does give, and substituting these in Equation 3a the curves of Figs. 5 and 6 have been calculated. The points shown are the experimental data given by Mariller. Inspection of these figures shows that the equations correspond in type to the experimentally determined results.

PLATE EFFICIENCY

It is obvious that in practice equilibrium will not be reached between vapor and liquid. The number of plates actually needed for a given enrichment divided into the number theoretically necessary according to these formulas may be called the plate efficiency of the column. This will obviously vary with type of construction. If in a given column, with a given overflow and a given vapor rate, the plate efficiency, k, is otherwise constant from plate to plate, as is not improbably the case, this quantity k may be multiplied into Δn in Equation 3a or Δm in Equation 4, and these equations then become applicable to actual columns. It is necessary only to determine from experimental operating data upon existing columns the influence upon k of type of plate, rate of flow of vapor and of reflux, etc., in order to be able to use these equations in problems of column design with safety and assurance.

APPLICATION OF FORMULAS—DESIGN OF CONTINUOUS RECTIFYING EQUIPMENT

In order to illustrate the value and method of use of these equations the following typical example is worked through.

It is desired to rectify continuously a 10 per cent alcohol solution to produce a 94.5 per cent product and leave only 0.1 per cent alcohol in the waste, using the type of equipment shown in Fig. 1. What overflow should be used? What will be the height of the column required and at what point should the feed be introduced?

The best amount of reflux depends upon an economic balance between overhead charges and operating cost. This can be determined only by a knowledge of the relation between the amount of overflow and the number of plates required. The value of k has been assumed constant and equal to 0.8. Four different amounts of overflow have been assumed, *i. e.*, 3.8, 5, 10, and 20 moles per mole of product, and for each the number of plates required determined. Complete methods are shown for the second case (5 moles overflow per mole of product) and all others have been calculated similarly.

Fig. 7 shows the minimum overflow as calculated for various points in the column above the feed plate. Inspection shows that unless the feed is introduced at a point lower than $x = 0.028$ the minimum overflow will be 3.00 moles, representing the minimum allowable at $x = 0.835$. The minimum overflow below the feed plate is not shown, as calculation later shows that any overflow sufficient above the feed plate, together with the feed itself, is more than the minimum overflow below the feed.

Knowing k, and assuming a value of 5.0 for O, Figs. 8, 9, 10, and 11 have been calculated from Equations 3a and 4, and graphic integration under these curves gives the required x vs. n curves of Fig. 12 which are enlarged in Fig. 13 in the neighborhood of the feed plate.

Especial attention must be given to Fig. 9, which shows the reciprocal of the rate of enrichment as one goes up the column. Note that the enrichment curves for the bottom

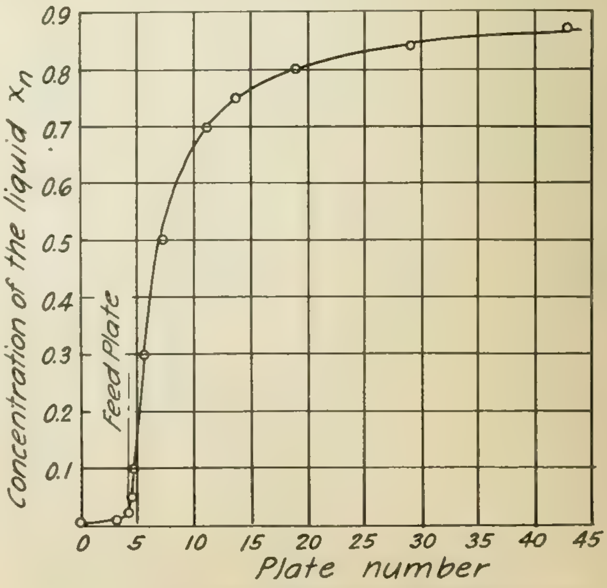

FIG. 12—CALCULATED VAPOR AND LIQUID ENRICHMENT IN COLUMN. PROBLEM O = 5.0 MOLES

and top of the column cross at $x = 0.02$. If the feed enters on a plate in the column on which the concentration is greater than this, then from the feed plate down to that plate on which $x = 0.02$ the enrichment rate is lower than it would be were the feed brought in lower down. Similarly, if the composition on the feed plate is less than 0.02, from the feed plate up to $x = 0.02$ enrichment rate is sacrificed. Hence the feed should enter the column on that plate at which the enrichment curves for bottom and top of the column intersect, as otherwise efficiency of utilization of the plates is sacrificed. So far as is known to the writer, this is the first method ever offered for determining at what point the feed should enter a column. It would seem that in commercial practice the feed is often introduced too high up the column.

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[4] "Distillation Fractionée et la Rectification," Paris.

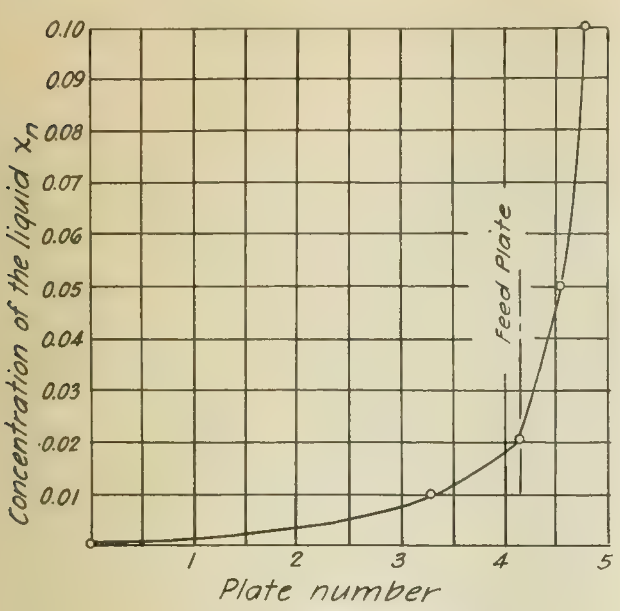

FIG. 13—CALCULATED ENRICHMENT AT THE FEED PLATE. PROBLEM O = 5.0 MOLES

Fig. 14, constructed from Table II, shows the influence of amount of overflow, or, what is equivalent to the same thing, heat consumption per unit amount of distillate upon the number of plates required in the column. It has already been pointed out that in this particular case an overflow of at least 3 is required and this would involve a column of indefinite height, *i. e.*, the curve is asymptotic to an overflow of 3. An overflow of 4 requires 67 plates. An overflow of 6, however, reduces the plates to 36. An overflow of 20 requires 25 plates, and it is obvious that still larger overflows will save almost nothing in column construction. Intelligent design requires an economic balance between the cost of the column and that of the heat required to operate it and such a balance can immediately be struck from this curve once the cost of plates and of steam is given. Once Curve 14 is constructed, the choice of the proper height of column for the case in hand becomes a mere matter of cost accounting.

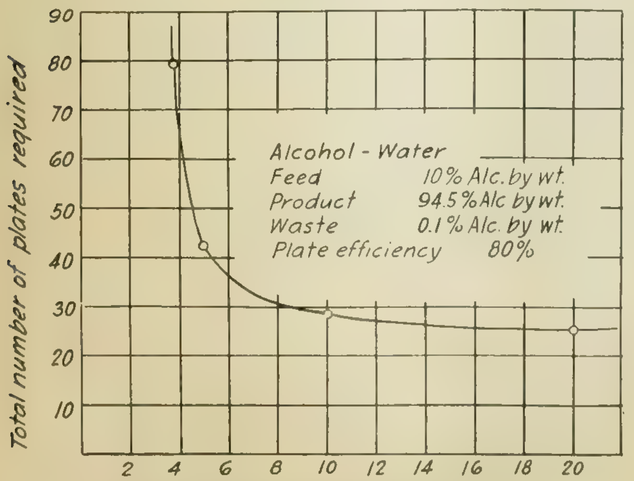

FIG. 14—EFFECT OF AMOUNT OF REFLUX ON THE NUMBER OF PLATES NECESSARY FOR A GIVEN RECTIFICATION

It will be remembered that while Equations 3*a* and 4 are rigidly accurate, they have been used with the simplifying assumption of constant molal overflow. This is not, however, necessary in actually using them. Calling the total heat of vaporization represented in the vapors from the n^{th} plate Q_n, and the *molal* heat of vaporization of the more volatile component r_1, and of the less volatile r_2, then

$$Q_n = V_n\,(r_1x_n + r_2(1-x_n)).$$

Furthermore, neglecting change in temperature of liquid and vapor from plate to plate, this quantity is constant, though with a different value below the feed plate than above if the feed is below its boiling point. Remembering that $V_n = O_{n+1} + V_c$, there results

$$O_{n+1} = Q_n/(r_1x_m + r_2(1-x_m)) - V_c.$$

This value of O_{n+1} can be inserted in Equation 3*a*, and these equations used for mixtures of any two liquids. If desired, weight quantities may be used instead of moles throughout, but the molal method is simpler where molal heats of vaporization are identical. If the refinement is required, correction can be made for the temperature changes in the column by reference to the boiling point curves.

TABLE I—GRAPHIC METHOD OF INTEGRATION UNDER *dn/dx* CURVE FOR DETERMINING NUMBER OF PLATES REQUIRED FOR RECTIFICATION

Problem: overflow = 5.

FROM $x =$	TO y_2	AREA Sq. In.	1 Sq. In. Equals	Δn	n
Below the feed					
0.0004	0.010	4.11	0.8 plates	3.29	3.29
0.010	0.0205	2.08	0.4	0.83	4.12
Above the feed					
0.0205	0.0500	1.02	0.4	0.408	4.53
0.05	0.10	0.59	0.4	0.236	4.76
0.10	0.30	0.23	4.0	0.92	5.68
0.30	0.50	0.39	4.0	1.56	7.24
0.50	0.70	1.00	4.0	4.00	11.24
0.70	0.75	0.61	4.0	2.44	13.68
0.75	0.80	1.33	4.0	5.32	19.00
0.80	0.84	2.50	4.0	10.00	29.00
0.84	0.87	3.45	4.0	13.80	42.8

TABLE II—EFFECT OF AMOUNT OF REFLUX ON THE NUMBER OF PLATES NECESSARY FOR A GIVEN RECTIFICATION

Overflow	3.8	5	10	20
Plates required above feed	73.5	38.7	26.8	24.4
Below feed	5.6	4.1	1.7	1.0
TOTAL	79.1	42.8	28.5	25.4

23rd Chemists' Exhibition

The 23rd Chemists' Exhibition will be held at the Central Hall, Westminster, facing Westminster Abbey, London, S. W., on June 19 to 23, 1922.

The Exhibition will consist of a comprehensive display of drugs, chemicals, and allied goods. It is attended each year not only by the pharmacists of Great Britain and her overseas possessions, but also by men from foreign countries interested in the drug and chemical trades.

A contract has been let for a new chemistry building at the University of Saskatchewan, Saskatoon, at a cost of $650,000. Construction work has already begun, and the building is to be completed by July 1, 1923.

The U. S. Government Explosives Plant C, Nitro, West Virginia[1]

II—The Manufacture of Sulfuric Acid by the Contact Process

By **March F. Chase**[2] and **F. E. Pierce**

L. L. SUMMERS & CO., 140 NASSAU ST., NEW YORK, N. Y.; F. E. PIERCE, 119 BROAD ST., NEW YORK, N. Y.

As one of the requirements of a completely integrated smokeless powder plant was the building of a sulfuric acid plant, it became necessary to decide on the process and type of plant to be used.

Sulfuric acid is produced commercially by two well-known general processes, usually designated as the contact process and the chamber process. Where it is desired to produce an acid stronger than 60° Bé., the contact process is ordinarily used; otherwise large concentrating units must be built.

Aside from requiring in powder manufacture sulfuric acid of high acidity, arrangements must be made to fortify the weak sulfuric and nitric acid that is recovered from the nitrating process. The contact process would seem better adapted for the purpose, but the chamber process with concentrating units, being generally better known, had many staunch advocates in the discussion preceding the decision of the question. It was finally decided to build a contact plant. After this decision, the specific type of plant had to be considered from the standpoint of speed of construction and quantity of platinum to be used. It must be remembered that platinum was very difficult to obtain at this time. The story of how it was obtained is one of intense human interest, but has no place in this article.

SELECTION OF PROCESS

The process selected was the Schroeder-Grillo process. This really means that the Schroeder contact mass was used, as there is really no such thing as Schroeder-Grillo contact process. The contact method of manufacturing sulfuric acid consists in brief of the following steps:

1—The production of burner gas containing sulfur dioxide from brimstone or a suitable sulfur-bearing ore.

2—The purification of the burner gas by scrubbing and filtering.

3—The oxidation of sulfur dioxide to sulfur trioxide by intimate contact with finely divided platinum.

4—The absorption of sulfur trioxide in sulfuric acid.

Contact sulfuric acid units having a capacity of approximately 2000 tons H_2SO_4 per month are the most economical of operation because they are well balanced from the standpoint of operating labor, the duties of the operators being principally that of observing the working of the process. A large plant does not require proportionately as many men as a small plant. As the life of plant equipment is greater when in daily operation than if run spasmodically, it is well to have the units selected with such capacity that continuous operations may be possible.

Brimstone is the ideal crude material for economical operation; as it was obtainable it was decided to use it as the source of sulfur. An additional advantage in using it is that the quantity required for any given production is considerably less than that required when other sulfur-bearing materials are used.

With the above points in mind, it was finally decided to build seven units consisting of four systems each. (Figs. 1 and 2.) The normal capacity of each unit was 80 tons H_2SO_4 per day or 2400 tons per month. The units put in initial operation produced from 2700 to 2900 tons per month. The selection of the type of buildings was determined by two factors; the nature of the process and the apparatus to be used, and the very limited space available for this part of the plant. It was essential that the buildings be made fire-resistant, if not fireproof.

The converter building had a steel frame with tile walls, cement tile roof, and steel sash. The absorber buildings were timber frame with tile walls and roofs of sheathing, covered with prepared roofing. The total floor space required for the entire seven units was something under 300,000 sq. ft. and the total cubical contents about 7,500,000 cu. ft. The first unit was started on March 15, 1918, and completed on June 10, 1918. At the time of the Armistice four units were 100 per cent completed and the balance about 96 per cent.

PLANT AND PROCESS

The brimstone is brought in carload lots and unloaded into concrete sulfur storage bins, from which it is carried by wheelbarrows to the burner building, weighed, and dumped into the hoppers of the burners. The burners are Glens Falls sulfur burners, 4 ft. in diameter by 16 ft. long. Each unit is equipped with four burners, one for each system. A cast-iron combustion chamber follows the burner. After passing through the combustion chamber, the gas passes through large cast-iron pipes for the purpose of cooling the gas before it reaches the cooling tower. From the last vertical pipe in this cast-iron cooler, the sulfur dioxide gas passes through what is called the No. 1 lead tower. This tower is 8 ft. square and 20 ft. high, made of lead, lined with 4 in. of acid-proof brick and filled with quartz. The gas entering this tower is still quite warm. Use is made of this heat to concentrate the acid, at the same time cooling the sulfur dioxide gas. This tower is sprayed with the acid coming from the dry towers. The tower is provided with the customary acid coolers and acid pumps. The gases leave the first lead tower and pass through a water-sprayed sulfur dioxide cooler, consisting of 16-in. lead pipes 45 ft. long, connected so as to form a coil four pipes high and four wide. From these flues the gas passes into the No. 2 lead tower, which is of similar construction and alongside of the No. 1 tower. The No. 2 tower is sprayed with 60° Bé. acid and is used for the purpose of drying the gas. The discharged acid from this tower is returned to the top of the No. 1 tower, and in passing through is concentrated so that it can be used on top of the No. 2 tower. It is difficult in this operation always to balance the two towers completely, so that at times there is some accumulation of acid which has to be removed and at other times a small amount of stronger acid from the absorbing system has to be added for the purpose of bringing up the acid in the tower circulating systems to the proper strength.

From the No. 2 lead tower, the sulfur gas is piped to the coke filter through a lead line. The pipe for each unit is

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[1] Received April 24, 1922.

[2] M. F. C., Consulting Engineer. Formerly Assistant Director of U. S. Government Explosives Plants; formerly member of War Industries Board. F. E. P., Consulting Engineer, and with Pierce & Skogmark, Inc., Consulting Engineers on U. S. Explosives Plant C, Sulfuric Acid, Nitro, Va.

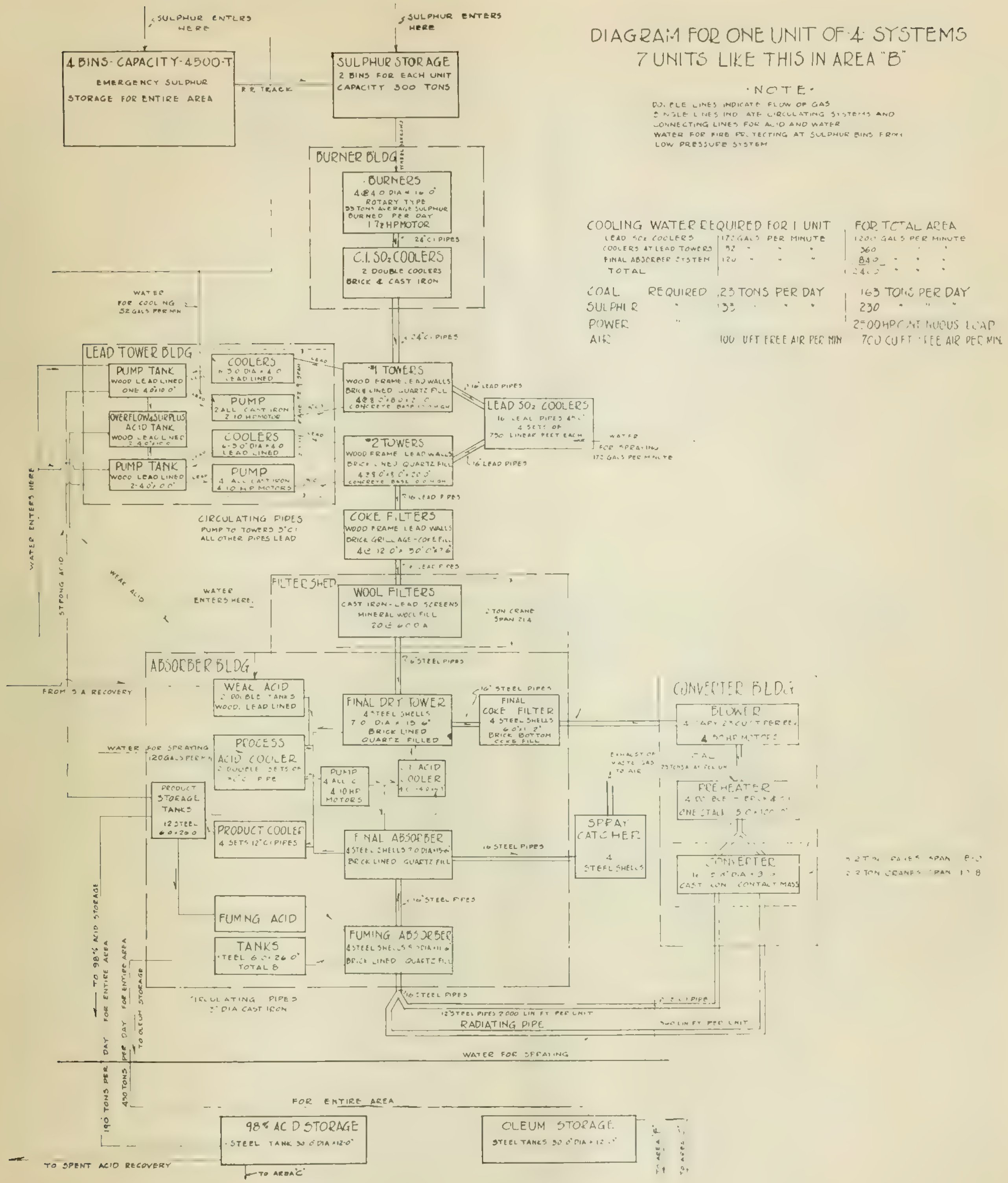


FIG. 1

carried from the top of the No. 2 lead tower to the roof of the converter building on a structural steel platform, the clearance under this platform being 35 ft. The coke filters are lead boxes reinforced with timbers. They are 30 ft. long, 12 ft. wide, and 10 ft. high, and are filled with coarse coke at the bottom and 3 or 4 ft. of fine coke at the top. The gases pass upward and lengthwise of the box. From this point the gas is taken through a 16-in. lead pipe to the mineral wool filters. These filters are of cast iron 6 ft. in diameter, and five are used on each system. Inside these filters are two lead screens supported by lead covered pipes. On each screen is a layer of cotton fiber about 1 in. thick and one of mineral wool 8 in. thick. The gases pass downward through the filter and are discharged through 8-in. pipes into a 16-in. header. In operation, the filter material is removed from time to time and fresh mineral wool added. From these filters the gas is taken through a steel pipe to the final dry tower. The gas enters near the bottom and passes

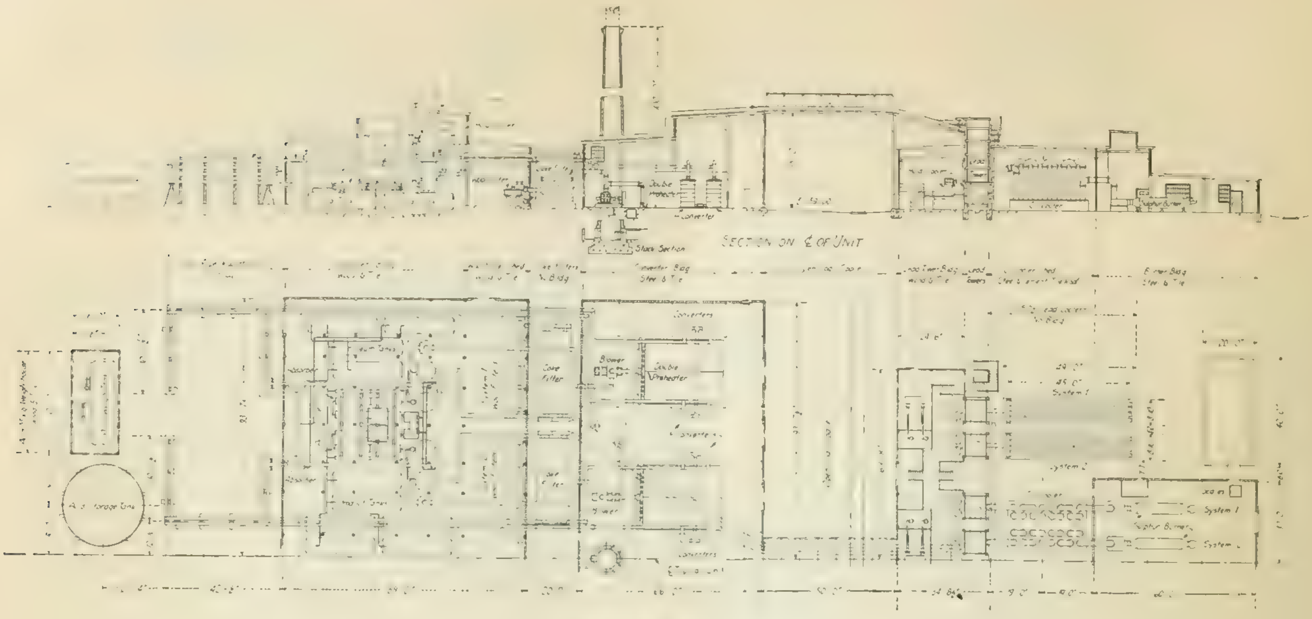


Fig. 2—Area B, Typical Unit Half Plan and Section

upward through the tower, which is sprayed with 98 per cent acid during the process. From the final dry tower the gas is taken through a steel tower, filled with coke for the purpose of eliminating any acid that might be mechanically carried along in the gas. From here the gas is passed to the blowers.

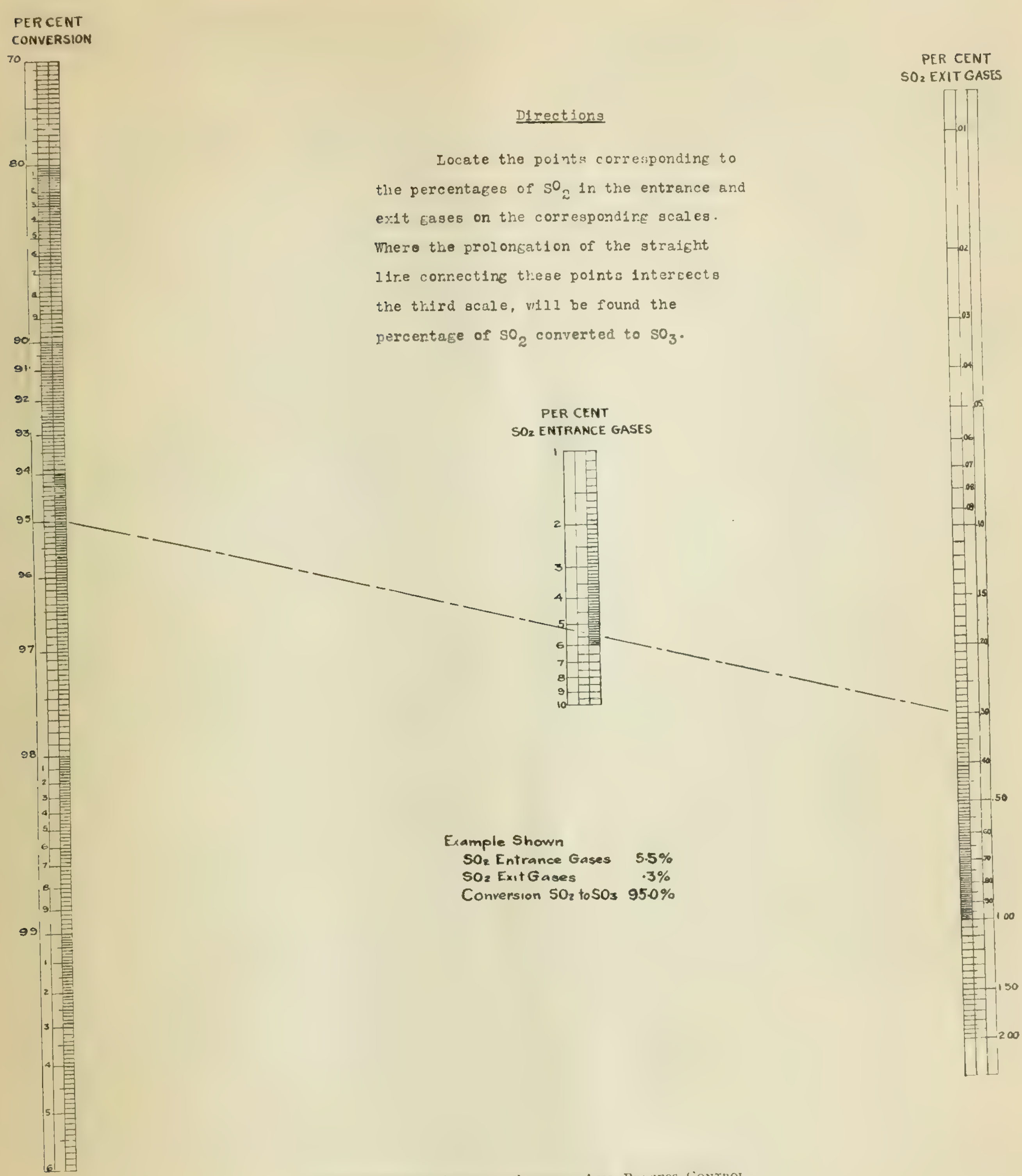
Up to this point in the process the movement of the gas has been caused by suction produced by electrically driven blowers of 3000 cu. ft. per min. capacity each, there being one blower to each system. From this point in the system the gas is moved onward by the pressure from these same blowers. The gas is now free from moisture and solid impurities and is ready for conversion into sulfur trioxide. Each system is provided with one double preheater, heated by two gas burners. These preheaters consist of a brick setting and contain two combustion chambers and two heating chambers. Each heating chamber contains a series of cast-iron U-pipes. The sulfur gas enters these pipes from a header running across the front of the heating chamber and passes out at the rear through a similar header. In the preheaters the sulfur gas is heated to a temperature of approximately 400° C. After heating, the gas passes through the converters which contain the contact mass. There are four converters to each system and each converter contains five layers of contact mass. These converters are ordinary shelf converters and no attempt is made to utilize the heat of the reaction after preheating the gas. While this can be done with considerable economy by means of a heat interchanger, it was thought advisable, on account of the necessity of rapid construction, not to go into the more or less elaborate designs required to accomplish the saving of the heat. The converters are such as had been used for several years at different plants, and it was known from past experience just how they would work and how much platinum would be required in them. A saving of a considerable amount of platinum and quite a few days in the time of completion of the plant was accomplished through using this particular style of converter.

The gas leaves the converters at a temperature between 500° and 550° C. It is conducted from the converters through pipe lines, the first part of which are of cast iron and the latter part of steel, to the radiators, which are in the open air adjoining the absorber building. Sufficient radiating surface is provided to bring the gas to the fuming absorbers at the proper temperature for absorption. The fuming absorbers consist of steel shells 5 ft. in diameter and about 11 ft. high, filled with quartz. These towers are sprayed with acid which is passed through the tower a number of times until the proper strength is reached. They are designed to produce acid of 106 per cent H_2SO_4. It was found that ten passes of the acid during a 24-hr. period would produce acid of this strength. The second fuming absorber was added later on for the purpose of bringing the strength to 109 per cent. Under this plan the sulfur trioxide gas from the top of the first fuming absorber is piped to the bottom of the second fuming absorber, passes through it, and is led to the final absorber. The acid from the first fuming absorber is circulated through the second until it reaches a strength of 104 per cent, after which it is recirculated through the first absorber until the desired strength of 109 per cent is reached. In order to get the best possible results in the production of fuming acid, it is necessary to cool the acid that is used for spraying and fuming absorbers.

From the fuming absorbers the gas goes to the final absorbers, which are ordinary steel tanks 7 ft. in diameter and 15 ft. high, lined with acid-proof brick and filled with quartz.

Following the final absorbers, the gas is led through spray catchers to catch any spray carried over mechanically. These final absorbers are sprayed with acid running from 99 to 100 per cent H_2SO_4.

With proper regulation of the temperature of the acid and of the gas entering the absorber, it is possible to get practically complete absorption. The absorbing acid is kept at constant strength by the continual addition of weak acid obtained from the recovery system of the spent acid plant. The excess acid flows off automatically through a 12-in. pipe which is cooled by spraying and led to the storage tanks. In order properly to gage the output of acid, weigh tanks are provided for weighing the weak acid delivered to the plant and the strong acid produced. In ordinary practice the figures of output are arrived at by measuring the acid in the tanks, but this involves some errors which it was deemed



Directions

Locate the points corresponding to the percentages of SO_2 in the entrance and exit gases on the corresponding scales. Where the prolongation of the straight line connecting these points intercects the third scale, will be found the percentage of SO_2 converted to SO_3.

Example Shown

SO_2 Entrance Gases	5.5%
SO_2 Exit Gases	.3%
Conversion SO_2 to SO_3	95.0%

Fig. 3 Conversion Chart of Sulfuric Acid Process Control

best to obviate in this particular installation by installing scale tanks.

Strong acids freeze at fairly high temperature. To provide against this contingency in operating in cold weather, tanks were provided for holding anti-freeze mixture, which is a mixture of sulfuric and nitric acids. This anti-freeze mixture is used in mixing with the various strengths of oleum produced which have a high freezing point.

Throughout most of the plant the acid is handled by ordinary cast-iron centrifugal pumps. In transferring acid from some of the storage tanks it was found that this could be done easier by blowing with compressed air. For this purpose three electrically driven two-stage air compressors are provided.

Chemical Control of Process

The entire process is checked regularly by chemical analyses; the gas entering the preheater is tested every 2 hrs. for sulfur dioxide content, the suction pressure and speed of the blower being taken at the same time. The acid used for spraying the lead towers and the absorbers is maintained at the proper strength by continual testing with hydrometers. The strength of the strong acid for the absorbing tower not being readily determined in this way, recourse was had to a system of proper dilution so that the diluted acid could be tested with a hydrometer and the exact strength of the original acid determined by reference to a table. This provides a quick, accurate and easy method of determining the exact strength of the acid when the acidity is between 93 and 100 per cent. An easier way of doing this, however, is by an electrical method which is used in a number of commercial plants. Apparatus for this was not available at the time the Nitro plant was constructed.

CONTACT MASS

The contact mass is calcined magnesium sulfate impregnated with platinic chloride. This mass is prepared by calcining pure epsom salts and crushing and screening the product. The part going through a 0.25-in. screen is reworked and that going through a 0.75-in. screen is recrushed. The mass which is of proper size is sprinkled with a dilute solution of platinic chloride of such a strength that the percentage of platinum in the mass varies from 0.15 to 0.30 per cent. The mass containing the greater amount of platinum is placed in the section of the converter in which the sulfur gases first enter. Before passing sulfur dioxide gas through the converter, hot air is circulated through the mass. Upon heating, the platinic chloride breaks down, giving off chlorine gas and leaving a gray, finely divided platinum. The magnesium sulfate is, of course, used simply as a binding material or carrier to present the platinum in a form in which it can act on the sulfur dioxide.

The combustion gases entering the converter contain about 5.5 per cent sulfur dioxide, the balance being made up of oxygen and nitrogen. The formation of sulfur trioxide in the presence of the platinum is caused by the reaction of some of the oxygen which entered the system at the burners and which has traveled to this point without uniting with the sulfur dioxide.

It was intended that 0.266 oz. of platinum per lb. of sulfur burned per hr. should be used. On account of the difficulty of maintaining a proper conversion with new operating forces, it was afterwards deemed advisable to increase this by about 40 per cent. Even the revised ratio is considerably lower than that used at many other plants, as will be seen by reference to Table I. While the purification system used is probably somewhat more expensive than that which might be installed, it is compensated for in a large degree by the saving in platinum.

TABLE I—PLATINUM USED AT VARIOUS PLANTS

	Sulfur Burned Lbs. per Hr.		Average Platinum in Mass, Oz.		Ratio of Sulfur Burned Oz. = Pt/Lb./Hr.	
PLANT	Original	Revised	Original	Revised	Original	Revised
A	1000		0.30		0.438	
Nitro	750	750	0.16	0.20	0.266	0.373
B	1000		0.20		0.437	
C	1000		0.30		0.416	

A total of 85 days of field work for constructing completely a 100-ton sulfuric acid plant was somewhat of an undertaking, but as rapid as this may seem, it had been excelled before, by the du Pont Company at their Hopewell plant. The size of the unit was not as large, but the actual time of field work was considerably less. The two construction jobs cannot be very well compared on account of the different conditions under which they were done, but taking everything into consideration, the accomplishment was quite remarkable.

Efficiency, from the standpoint of sulfur consumption, was slightly sacrificed for a saving in platinum. Saving in fuel by installing regenerative converters was not considered on account of the time involved in procuring proper regenerative converters. This defect in the plant is one that could be readily corrected at any time.

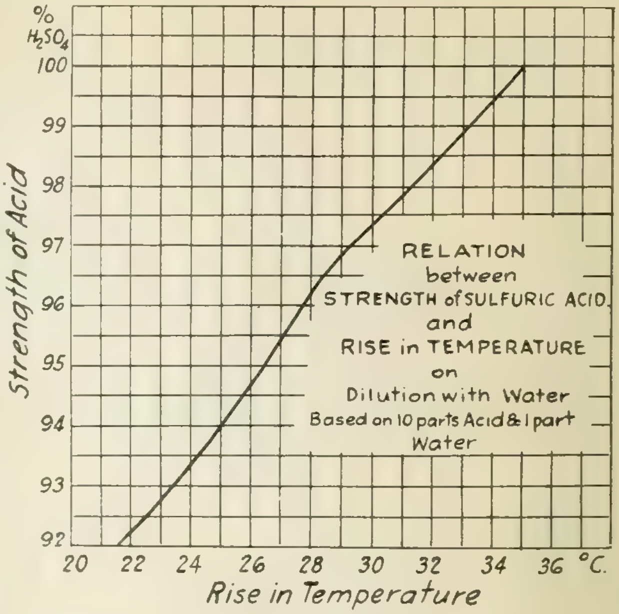


FIG. 4

The heat of combustion developed in the formation of sulfur dioxide in the sulfur burners could also have been utilized in the preheater, with a result in saving of fuel. In this case, the sulfur burners would have had to be placed in proximity to the preheaters. As it was not certain whether the plant would be operated at all times on sulfur, it was thought advisable to instal complete scrubbing equipment and so to place the sulfur burners that pyrite burners could be substituted, if necessary.

The strength of oleum produced depends upon the temperature of the gases which are absorbed and the percentage volume of sulfur trioxide in the gas. On account of the enormous amount of weak sulfuric acid that was to be recovered from the nitrating process, it was thought advisable to produce the greatest quantity of highest strength acid possible. This meant the treating of a gas high in sulfur dioxide: first to cut down the amount of water taken into the system and, second, to provide as high sulfur trioxide content as possible in the gas to be absorbed. By reference to Table II it is seen that the relative amount of water introduced through the air is greatly increased as the strength of the sulfur gas decreases and the temperature of the air rises.

TABLE II LBS WATER PER DAY WHEN BURNING 1000 LBS. OF SULFUR PER DAY WITH SATURATED AIR

TEMPERATURE	Per cent SO_2				
° F.	4	5	6	7	8
52	185	160	140	115	90
62	255	225	195	165	135
72	370	325	280	235	190
82	515	450	390	325	260
92	710	630	540	445	360
102	980	855	730	605	490

In the above description acid having a strength greater than 100 per cent has been mentioned. This refers to oleum or fuming acid. These percentages are easily reduced to per cent fuming by use of the following formula:

$$\frac{\text{Per cent } H_2SO_4 - 100}{0.225} = \text{Per cent fuming}$$

In figuring the per cent of sulfur dioxide converted, the following formula is used:

$$c = \frac{10,000\ (a-b)}{100a - \frac{3ab}{2}}$$

where
a = per cent SO_2 in entrance gas,
b = per cent SO_2 in exit gas, and
c = per cent conversion.

A chart for readily determining the per cent of conversion where the per cent by volume of sulfur dioxide in the entrance gas and exit gas is known is illustrated in Fig. 3.

Fig. 4 is used for determining roughly the strengths of acid by measuring the rise in temperature in ° C., upon rapid dilution with water. The curve shown is based on diluting 10 parts of acid whose strength is to be determined with 1 part of water.

Investigation of Whitewashes and Aqueous Lime Paints[1]

By G. J. Fink

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Exposure tests of one hundred and seventy-five formulas for whitewashes and aqueous lime paints have been made. Definite data and illustrations are presented showing the effects of a large number of ingredients in various combinations and conclusions given regarding the relative merits of the various formulas.

Of the siccatives used those such as casein, which with lime form insoluble films, proved to be the best. Water-soluble siccatives such as glues are not so satisfactory for exteriors. Several alkaline salts were used for accelerating the solution of casein, trisodium phosphate proving to be the most satisfactory. Among the addition agents used with lime in mixtures containing no definite siccative, alum and table salt were effective in improving the workability and permanence of the whitewashes. Several formulas developed and tested are shown to be superior to most of those in common use.

WHITEWASH or a milk of lime suspension is one of the most ancient and most widely used of the class of paints in which water is the chief vehicle. In its simplest form, whitewash is prepared by mixing slaked lime with water. Such a mixture possesses good covering power, produces a very white film when properly prepared, is cheap, and easily applied, and owing to these properties has a wide field of usefulness distinct from that of oil paints.

However, as a result of endeavors to improve the simple formula and to develop aqueous lime paints which would have special properties and lend themselves to special uses, there exist at the present time a surprisingly large number of formulas.[2] In addition to the simpler mixtures for painting of cellar walls, fence posts, and accessory buildings about the farm, we have the modified and more specialized formulas for such purposes as the temporary marking of obstructions along highways; the painting of fruit tree trunks for prevention of early budding, and as a deterrent of the root borer;[3] the prevention of rust on certain types of steel structures;[4] for fireproofing and assisting in the lighting of certain centers of activity in mines; the coating of the inside of boat hulls to prevent decay; the protection of concrete against the action of oils and other fluids;[5] as calcimines and tints for interior decorating; as heat-resistant and fire-retardant paints for wood[6] and fabrics;[7] and a large number of other purposes which could be enumerated. Outside of the formulas given in texts on paints and in certain recipe books, the information relating to the wide variety and range of application of lime paints is protected as company secrets or is confined to the patent literature and is not a matter of general or common knowledge.

In the numerous formulas a large number of addition agents are mentioned, each having been used to give the paint certain desired properties or to make it applicable for some particular purpose. These addition agents include agglutinous materials or siccatives such as milk, prepared casein, albumin, glue, grain flours, resins, gums, and vegetable oils; salts such as sodium chloride, sodium carbonate and bicarbonate, borax, alkali phosphates, etc., which are effective as precipitants or in increasing the solubility of the lime or siccative; substances such as the sulfonates of benzene and naphthalene which are supposed to facilitate the solution of glue in certain formulas; pigments other than lime such, for example, as whiting, zinc oxide, and lithopone; and finally the so-called preservatives for the organic matter, among which are carbolic acid, alum, zinc salts, arsenic compounds, thymol, naphthalene, salicylic acid, most of which probably have the effect of hardening and rendering the organic matter insoluble rather than exerting the supposed simple preservative action. Many of these mixtures may be prepared and marketed as dry powders and are made ready for application simply by mixing with water. Others must be prepared on the job.

A search of the literature fails to reveal a record of comparative tests of recommended formulas and there are very few published experimental data relative to the theoretical considerations involved in the use of a number of these addition agents or their relative values in terms of increased durability or special properties of the paint. This investigation was undertaken for the purpose of obtaining such data and of developing, if possible, simpler or more permanent formulas.

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[1] Received March 13, 1922. Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] For a collection of the more commonly used mixtures see: "Whitewash and Cold Water Paint," *National Lime Assoc., Bull.* **304**; "White Paints and Painting Materials," Scott, Painter Publishing Co., Chicago; "Paint and Color Mixing," Jennings, **1915**, Spon & Chamberlin, N. Y.; "Paint Making and Color Grinding," Uebele, **1913**, The Painters Magazine, N. Y.; "Manufacturers' Practical Recipes," Jameson, Vol. I (1902); "A Treatise on Color Manufacture," Zerr and Rubencamp, translated by Mayer, **1908**, Charles Griffin & Co., Ltd., London; "Dictionary of Chemicals and Raw Products," Hurst, **1901**, Scott Greenwood & Co., London; "Casein, Its Preparation and Technical Utilization," Scherer; "Use of Paint on the Farm," Walker, *Farmers Bull.* **474**, U. S. Dept. Agr.

[3] Oregon Agr. Expt. Sta., Third Crop Pest and Horticultural Report, **1915–1920** (January 10, 1915), 70.

[4] M. Meigs, *Power*, **47** (1918), 483, *Concrete*, **10** (1917), 174, also *Can. Chem. & Met.*, **26** (1922), 13.

[5] Brit. Patent 169,258 (1921), and other English and U. S. patents.

[6] *Rail. Main. Eng.*, **16** (1920), 344.

[7] H. W. Wells, U. S. Patent 1,374,128.

EXPERIMENTAL

It was impracticable to make exposure tests of the several hundred whitewash and aqueous lime paint formulas collected, many of which involved duplications of principle; hence it seemed most desirable to study the effects of a large number of the more likely and logical of the addition agents and thus to gain information as to the principles involved. Two series of tests were made.[8] The first series comprised exposure tests of one hundred and twenty-one different aqueous lime paints prepared by mixing, both singly and in certain combinations, forty different substances with suspensions of slaked lime. Twenty-one of these mixtures represented formulas which were recommended either in the literature or in private communications. In addition, and for purposes of comparison, tests of four commercial water paints were included. The latter were purchased in dry form from local dealers and were made up according to the directions supplied with the particular preparation. The second series included tests of formulas which were devised upon the basis of information gained from the first test.

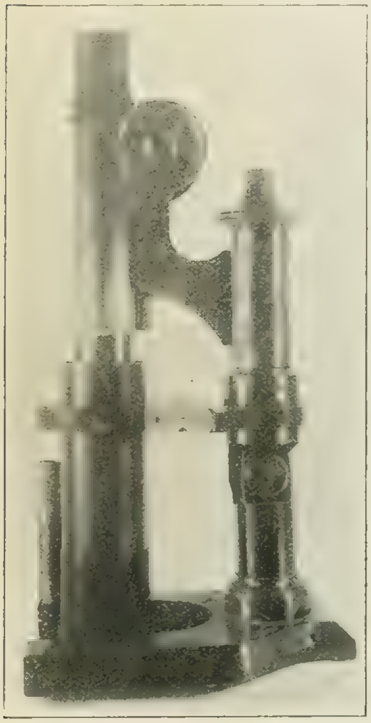

FIG. 1—INSTRUMENT FOR MEASURING RELATIVE CONDITIONS OF PAINT FILMS

PROCEDURE—Detailed procedure employed in preparation of each formula cannot be given here; in general, the mixtures were made by stirring, or incorporating by grinding, a solution of the addition agent into a paste made by thoroughly mixing 50 parts of hydrated lime with 60 parts of water. In certain cases where there was a tendency for the mixture to granulate as the result of precipitation of some reaction product, the substances were mixed in such order as to minimize this effect. For example, a mixture containing lime, casein, and soap was prepared by adding the solution of casein to the lime paste and stirring carefully into this the solution of the sodium soap. The calcium soap was thus produced in a very finely divided form yielding a smooth paint, the casein probably acting as a protective colloid. Casein mixtures containing a salt of alkaline reaction were made up by dissolving the casein in the solution of the salt and adding the mixture thus formed to the lime paste. Glue was always soaked in cold water and dissolved over a water bath. The proportions of addition agents indicated in the formulas were in a few cases arbitrarily selected, owing to lack of any information as to their possible reaction or effect, but in the greater number of mixtures the proportions were either those suggested by formulas already in use or were determined by the considerations involved, such as chemical reaction, workability of the mixture, hiding power, cost, etc. Very detailed data as to the methods of mixing, characteristics of each mixture, etc., have been recorded but cannot be presented here.

The lime which was used in all mixtures was a high-grade commercial hydrate purchased from a local dealer. The casein used was of the quality commonly used for cold water paints and satisfied the borax solubility test. The glue was a high-grade joiners' variety. The other substances employed were of the ordinary technical quality. The figures in the tables indicate the quantities used with 50 parts by weight of hydrated lime.

After mixing, the pastes were reduced to brush consistency by gradual addition of water until they worked satisfactorily on a test board. The boards on which the mixtures were painted for durability tests were 12 in. × 4 in. × $^7/_8$ in. of selected dry dressed cypress, and as uniform in respect to grain, heart, and sap as could be obtained. They were sandpapered just enough to remove any raised grain, and two black stripes 1.5 in. wide were painted across one side with a mixture of lampblack in shellac. The boards were then cut, making a small test piece 3 in. long with the black stripe across one end and another 9 in. long with the stripe across its center. All surfaces of the two blocks were then given one coat of the freshly prepared whitewash. After drying for 4 days, the longer boards were exposed on the roof[9] at an angle of 45°, exposure being to the south. Records of the tests included characteristics and workability of the mixture, nature of the dry film before exposure, index of relative hiding power of the dry film, and condition of the film after intervals of exposure of 10 days, 30 days, 6 wks., 2 mo., and 3 mo.

MEASUREMENT OF HIDING POWER—The index of the relative hiding powers of the original films and the figures representing the relative durability or condition of the test pieces at various intervals were obtained by the use of an instrument similar to that described by Hallett[10] for the determination of the hiding power of paints. The instrument used is shown in Fig. 1. It consists of the frame of a discarded microscope, to the tube of which has been fitted an extension which, by means of the regular microscope adjustment, can be raised or lowered inside the larger stationary tube. The inner tube is provided with a ground glass objective, and the ocular is simply a small circular opening. For a complete discussion of the theory of the instrument the article referred to above should be consulted. The method of operation is briefly as follows: The instrument is placed with the ground glass plate in direct contact with the surface, that is, the zero position. If the surface being viewed has two colors the two areas will appear quite distinct, but on raising the ground glass from the surface the contrast becomes less and less distinct until a point is reached at which the field appears to be uniform. The distance through which the objective has moved is a measure or index of the contrast between the two colors.

RELATIVE HIDING POWER—For determining the index of relative hiding powers of the dry whitewash films the instrument was placed on the small painted blocks in such a position that the edge of the black stripe, which of course had been partly or almost wholly obscured by the paint film, was in the center of the field as observed through the ground glass objective. If no contrast was shown between the black and the white, that is, if the black stripe was completely hidden, the reading on the scale of the instrument

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[8] A preliminary exposure test of twenty-four commercial formulas which were selected as among the most highly recommended and most widely used was made in this laboratory in 1920 by Mr. S. P. Armsby. Several modifications of these formulas were also tried out. These tests served to indicate the wide variation in the merits of the various mixtures and to suggest the need of an investigation of the principles involved in the use of the various addition agents.

[9] Mather Building, 918 G St., N. W., Washington, D. C.

[10] "An Instrument for Measuring the Hiding Power of Paints," *Proc. Am. Soc. Test. Materials*, **20**, II (1920), 426.

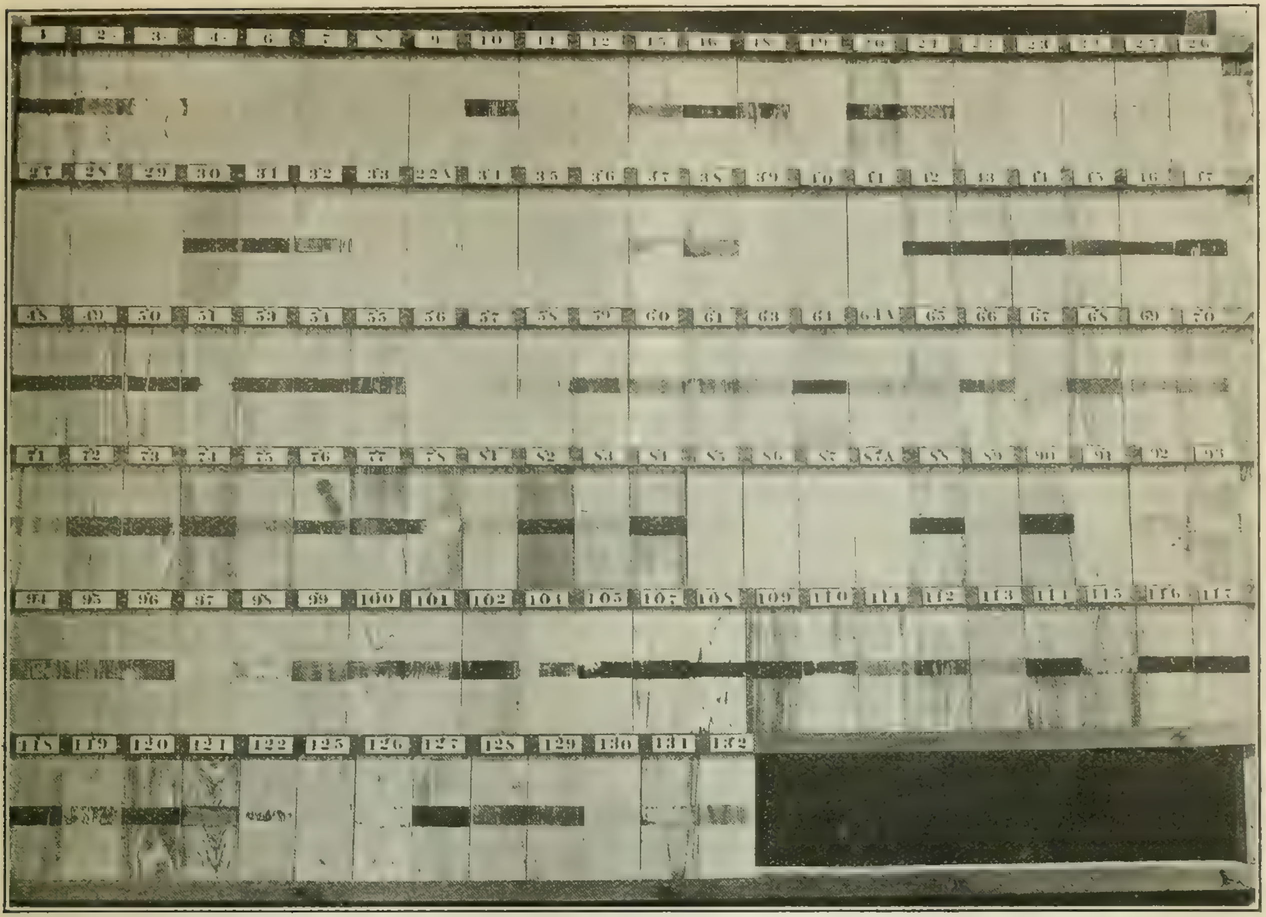

FIG. 2—APPEARANCE OF FILMS AFTER 6-WK. EXPOSURE. SERIES 1

was zero. However if the black was not entirely hidden, as was the case with the greater number of the films, the edge of the stripe was visible, and the objective was raised until the field became uniform. A reading of the scale thus becomes an index of the hiding power of this particular mixture as compared to some other. The relative hiding powers are inversely proportional to these index figures, that is, the film having the better hiding power has the lower index figure, and *vice versa*. No attempt was made to obtain an absolute value for the hiding power, as might have been done by a calibration of the instrument as described by Hallett. The index figures were considered sufficient for the desired purpose, that is, a comparison of the opacity or translucence of the different films.

RELATIVE WHITENESS—In order to obtain an index of the relative whiteness of the different films they were compared in turn with a black and a white. This was done in the case of the black by bringing a block which had been painted with drop black in contact with the whitewashed block and placing the instrument on the blocks in such a way that the juncture of the white and black appeared in the center of the field. Readings were taken as in the former case, the larger figures in this case indicating a whiter film, and *vice versa*. For comparison with white, a white paper was substituted for the black block, the paper being placed on the whitewash film and a measurement made with the edge of the paper in the center of the field of the instrument. The smaller figures in this case indicate greater whiteness. It will be noted that the range of variation in these two sets of values is not great, this being due to the fact that the great majority of the films were relatively quite white. A few, as indicated, were slightly transparent, and hence showed less contrast with the black standard and greater contrast with the white standard.

CONDITION OF FILM AFTER EXPOSURE—A measure of the condition of the film after exposure, *i. e.*, the amount of scaling, washing, etc., was obtained by determining the contrast of the portion of the film remaining with the wood exposed. Four readings were taken in a line across either end of the board parallel to the black stripe and half-way between the stripe and the end of the board, a total of eight readings, the sum being taken as the index figure. It is apparent that these values increase as the film weathers and pass through a maximum when approximately half of the film is off. Readings were taken at short intervals during the exposure tests, but only two sets are recorded in the tables. These values are not presented as absolute measures of the relative conditions of the various films, but they do, in the great majority of cases, check up with the general appearance of the test blocks, as shown by the photographs, and serve as a method of defining numerically something which is difficult to describe. Figs. 2, 3, 4, 5, and 6 are photographic records of the condition of the test blocks at stated intervals.

Space does not permit giving a complete list of the 174 formulas tested or a complete tabulation of the data recorded. In Tables I and II are presented the more important data obtained relative to the better and more typical formulas used. The figure following the chemical formula of the substance used indicates in the case of solids the number of parts of this substance per 50 parts by weight of hydrated

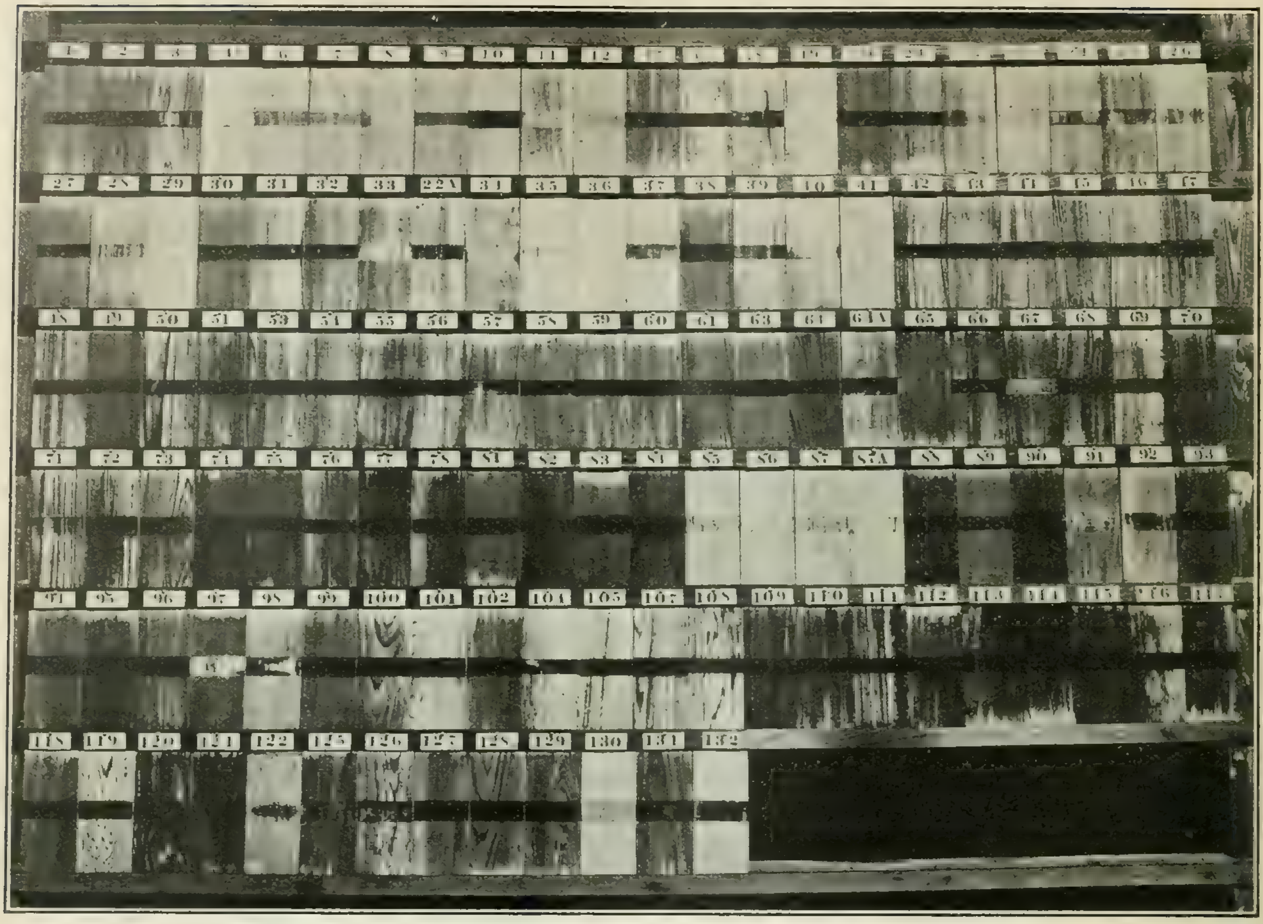

Fig 3—Appearance of Films after 3-Mo Exposure Series 1

lime, and in case of fluids the number of cubic centimeters per 50 g. of hydrate. The volume of water required to produce brush consistency was determined in each case but is not recorded in the table. This will vary somewhat with the lime used.

Discussion of Results and Conclusions

On the basis of the data recorded and observations of the condition of the films after exposure, attention may be called to the following more important facts. Formulas 1 (ordinary lime and water whitewash) and 44 (the commonly recommended lighthouse formula) may be taken as standards for comparison in showing the effect of various addition agents.

FIRST SERIES—The effect of vegetable oils in whitewash mixtures is shown in Formulas 1 to 16, inclusive. The addition of raw linseed oil alone to lime whitewash greatly reduces its hiding power but enhances slightly its durability (2).[11] The mixture is considerably improved by the addition of zinc oxide (3), and this formula is in turn greatly benefited by the presence of zinc chloride (4). The addition of a solution of casein to oil-lime mixtures (6–12) improves them quite markedly, but on the other hand nothing is gained either in workability or permanence by the use of oil in casein paints, the casein alone, as a siccative, being more effective than the combination. Such oil mixtures, however, tend to jel and for this reason are not so easily worked. Zinc oxide minimizes this condition to some extent. The films produced are not so hard as those produced by other formulas and tend to rub off slightly. The saponification of the oil by heating with the alkaline materials present brought about a slight improvement (10). China wood oil (18–19) gave slightly better results than linseed oil. Corn oil added to a simple lime whitewash seems to hasten deterioration (20), while cottonseed oil (21) improves it slightly.

Boards 22 to 41 were painted with casein mixtures. The beneficial effect of casein is quite positive, and the results through the entire series demonstrate it to be the best of the siccatives used in the tests.[12] Of the basic substances used to increase the solubility and fluidity of the casein, namely, ammonia, sodium carbonate, silicate of soda, caustic soda, borax, and trisodium phosphate, the last mentioned proved to be by far the best. Formula 29 clearly demonstrated this fact. This film was in relatively good condition after 5 mo. and at 6 mo. was only very slightly deteriorated. Block 33 was painted with a lime-casein mixture in which sodium silicate ("paint vehicle") was used to dissolve the casein. This did not show up well in this test, but in the second test in which it was duplicated (188) it did prove quite durable. Number 36, which proved exceedingly permanent, is a formula recommended by a manufacturer. Its general use under ordinary conditions, however, is not practicable on account of an exceptionally large proportion of casein, which introduces difficulties in getting ready solution and which adds materially to the cost.

[11] Numbers in parentheses refer to formulas listed in tables and figures.

[12] The use of casein in the form of skimmed milk in whitewash is a very common practice, and that milk curd, in combination with lime, has great cementing properties has been known to the initiated for centuries, Uebele, *Loc. cit.*, 375.

TYPE No	FORMULA PARTS PER 50 PARTS OF HYDRATED LIME(a)	WORKABILITY	CHARACTER OF ORIGINAL FILM				DURABILITY,- CONDITION AFTER EXPOSURE			
			APPEARANCE AND CONDITION	INDEX OF ORIGINAL HIDING POWER	WHITENESS.- INDEX OF CONTRAST WITH		SIX WEEKS		THREE MONTHS	
					BLACK	WHITE	INDEX OF CONTRAST WITH WOOD	APPEARANCE AND CONDITION OF FILM	INDEX OF CONTRAST WITH WOOD	APPEARANCE AND CONDITION OF FILM
1	Hydrated Lime alone	Fair	Uniform. White. Soft Chalks	4(l)	76(m)	0(l)	115(l)	Scaled About half off	(h)	Almost all off
2	Raw Linseed Oil 10	Good, Used thick	Transparent Soft, Rubs off	16	70	3	91	" badly	(h)	" " "
3	R Oil 12, ZnO 10	Better than °2	" " " "	12	72	3	75	" "	130	About half off
4	" 12, " 10, $ZnCl_2$ 2	Same as °3	Fair Rubs off slightly	14	76	B	36	Washed and transparent	72	Scaled and worn slightly
12	" 12, Casein 5, Na_3PO_4 3, HCHO 5(b)	Good	Trace yellow No Chalking	12	66	22	25	Incipient scaling	58	Worn slightly No large check
19	Tung Oil 12, ZnO 10	Works extra well	Very white Chalks slightly	10	80	0	36	A few fine checks	81	Worn on edges of grain
22	Casein 5, NH_3 10, Glycerine 5, Oil 12	Poor Separates	Separated Hard, No Chalking	24	36	23	55	Scaled Wood pigmented	84	Fine checks Worn
23	" 5, NH_3 10, HCHO 5	Good Gases Slightly	" " " "	8	72	12	32	Washed Fine checks	62	" " "
24	" 5, Na_2CO_3 3, " 5	Poor	Trace yellow Chalks Slightly	4	80	10	45	" " "	89	" " "
27	" 5, Borax 3, " 5	Good Spreads like oil paint	Fair " "	10	60	2	20	Slightly worn No scales	105	About half off
28	" 30, " 15, $NaOH_3$	Good. Sets rather rapidly	Fair Very hard and white No chalking	14	68	10	24	" " "	69	Badly worn
29	" 5, Na_3PO_4 3, HCHO 5	Fine Spreads like oil paint	" " " " "	2	80	0	(g)	Good condition	(g)	Good condition
40	" 5, Asbestine 5, Na_2CO_3 3	Fair Must be brushed out	Uniform Very hard	10	68	8	25	Worn Fine checks	68	Worn and checked
42	NaCl 15	Good	Good Rubs Slightly	14	64	12	85	Scaled along edges of grain	124	About half off Striped appearance
43	" 15, Glue 3	"	" " "	10	68	8	77	" " " "	107	" " " "
44(e)	" 15, Glue 1, Whiting ½, Flour 3	"	Slightly transparent Rubs slightly	44	60	12	66	" " " " "	110	" " " "
55	Glue 3	" Sets Rapidly	Good Hard Trace of Chalking	2	72	0	75	Worn No checks	125	Very thin About half off
56	" 3, HCHO 3	Excellent	Excellent Very hard No Chalking	6	70	0	62	" " "	120	" " Better than 55
64(f)	" 3, Na_2CO_3 2.5, Whiting 50, Oil 10	Good Slightly transparent	Slightly streaked Hard, No Chalking	44	70	12	112	Largely washed off	(h)	Almost all off Wood pigmented
64a	" 3, " 2.5, Oil 10	" " "	" " "	16	66	12	44	Worn slightly	121	Worn badly Much better than 64
66	" 8, Silicate 12, Whiting 100, Alum 8	Good	Good Very white Rubs Slightly	2	80	0	70	Badly Scaled	(h)	Over half off Wood pigmented
67(i)	Silicate 5	Sets too rapidly	" " "	20	68	4	95	Scaled and worn	(h)	" " " "
69	" 5, Na_2CO_3 3	Fair. Better than °67	Slightly yellow Fairly hard chalks slightly	40	56	12	71	Badly Scaled	128	About half off
72	Portland Cement 10	Good Sets rather rapidly	Gray Soft Chalks	8	64	6	100	" "	(h)	Over " "
77	Whiting 25	Good	White Soft, chalks readily	6	72	0	123	About half off Scaled	(h)	" " "
83	" 25, Na_3PO_4 4	"	Slightly yellow Soft, Chalks	12	66	2	83	Washed to thin film	(h)	Washed to very thin film
85	" 25, Casein 10, Na_2CO_3 6	"	" " Hard, Chalks slightly	8	70	3	(g)	Good condition	43	Slightly checked and worn
86	" 25, " 10, " 6, ZnO 10	"	Fair Very hard No chalking	14	64	3	(g)	" "	41	" " " "
87	" 25, " 10, " 6, HCHO 5	Fair Tends to Separate	Yellow " " " "	10	66	14	(g)	" "	37	" " " "
87a(j)	" 25, " 10, Na_3PO_4 6, " 5	Excellent	Excellent " " "	0	80	0	(g)	" "	(g)	Good Condition
88(k)	Soap 5	Good	Slightly yellow Soft chalks	10	68	12	98	Badly scaled	(h)	All off Wood pigmented
89	" 3, Casein 15, NH_3 25	Excellent	Slightly transparent, very hard no chalking	37	68	24	(g)	Very Transparent	(g)	Worn to very thin film
91	" 5, " 10, Na_2CO_3 6, HCHO 5	Good	Fair Med hard Trace of chalking.	12	66	6	20	Slightly Worn	85	Worn unevenly Thin in places
92	" 0.3, " 5, " 1, Borax 0.6	Fair	Poor Soft, chalks	16	70	8	42	Scaled Slightly	52	Worn and scaled Slightly Better than 91
94(c)	Flour 4	Good	White " "	8	72	4	107	Worn very thin	(h)	All off Wood pigmented
98	" 4, Na_3PO_4 3	"	Slightly yellow Hard, Trace of chalking	14	64	6	46	Slightly worn and checked	63	Slightly worn and checked
101	" 4, ZnO 10	Good Much better than °1	Good White, chalks slightly	6	76	0	40	Very white Worn	72	White Worn along edges of grain
104	$MgCl_2$ 5	" " "	Fair Chalks slightly	6	64	6	60	" " Scaled slightly	85	Very white Scaled
105	$CaCl_2$ 5	" " "	" Hard No chalking	8	80	0	41	" " " "	88	" " "
107	ZnO 10	" " "	Good Fairly soft, chalks readily	4	72	0	72	" " Badly scaled	95	Scaled and Worn White appearance
108	$ZnCl_2$ 2	Fair	" " " "	10	76	0	65	" " Scaled along grain	124	About half off
109	$ZnSO_4$ 2	"	" " " " "	8	74	8	(h)	Scaled Over half off	(h)	Scaled Almost all off
114	Kerosene 10	Fair Sets rather rapidly	Fair Soft Chalks	6	68	12	121	Scaled Almost half off	(h)	Almost all off
116	Alum 3	Fair Better than °1	Good Med hard Chalks Slightly	6	76	4	90	Scaled slightly	(h)	Scaled About half off
119	Glycerine 10	Good Much better than °1	Good White Soft, chalks	8	80	0	120	White Worn along grain	140	Off along grain. White
130	Commercial Cold Water Paint	Good	Good Slightly transparent Hard, No chalking	10	60	12	(h)	Good	25	Good Few fine checks

(a) Solids are indicated in parts by weight, liquids in terms of c.c. per 50 grams of lime
(b) Cubic centimeters of 40% Solution of Formaldehyde
(c) Rice flour used in all cases Paste made in usual way
(d) Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, used in all cases
(e). Lighthouse formula Allowed to stand 24 hrs and applied hot
(f) No 64 contains no lime. In 64a lime is substituted for whiting. Oil saponified by Na_2CO_3
(g). No figures are given if film is intact and wood is not exposed.
(h) No figures are given if film is over half off
(i). Sodium silicate paint vehicle
(j). Formaldehyde not in mixture, but was painted over dry film
(k). Flake soap used.
(l). Smaller values indicate better films
(m) Larger values indicate better films

TABLE I—TYPICAL FORMULAS. FIRST SERIES FIGS 2 AND 3

In Formulas 42 to 54, sodium chloride is the common constituent. The effect of the salt is very clearly indicated by the photographs. The simple lime-salt mixture (42) is a decided improvement over the straight lime wash. For-

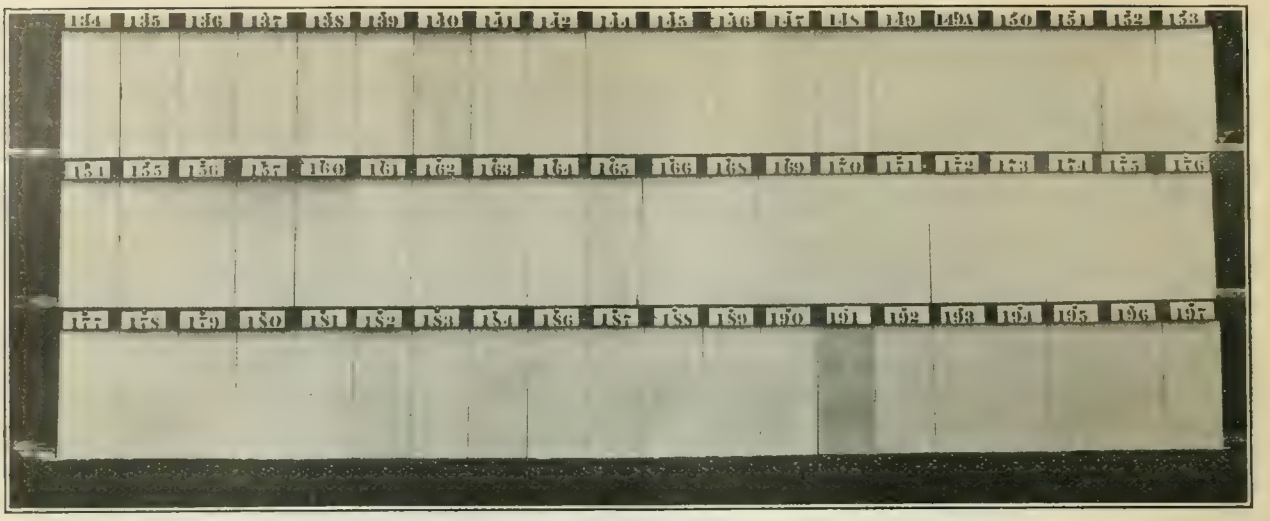

Fig. 4—Appearance of Films before Exposure. Series 2

mulas 43 to 54 are mixtures containing other components in addition to the salt, namely, glue, soda ash, borax, whiting, rice flour paste, soap, zinc oxide, zinc chloride, trisodium phosphate, asbestine, and various combinations of these materials. Very little improvement in permanence is gained by the use of these substances, some mixtures in fact being less permanent than the simple lime-salt combination. All of these formulas, however, show characteristic properties, which are the result of the common constituent. All the films deteriorated relatively rapidly during the first 6 wks. but showed little change during a second like period, a general white appearance or effect being preserved. For certain purposes, such as marking obstructions along highways where a permanently continuous film is not so essential and where the added cost of a more durable mixture is not justified, a simple salt formula finds a wide field of usefulness. These experimental results corroborate the practical experience of many users of whitewash.[13] The effect of salt is probably explained by the fact that it greatly increases the solubility of the calcium hydroxide, the degree of penetration of the lime into the wood thus being increased, and also by the presence of the soluble salt which tends to hold moisture and facilitate the carbonation of the lime. Number 44 of this series is the so-called government lighthouse formula which has been used quite extensively as an exterior whitewash. The results of these tests indicate that for exteriors the addition of flour and glue add little to the durability, and that many of the simpler formulas here given are better.

Formulas 55 to 66 have glue as their common constituent, 55 being a simple glue-lime mixture, while the others have in addition, separately or in combination, the substances used in the casein series. These glue films also show a common characteristic as to resistance to weathering. With one exception the deterioration is almost solely the result of solution or washing, and there is only a slight tendency to scale. The effect of the substitution of whiting for lime in a special case is shown in Formula 64, which contains no lime. Formula 64*a* is the same as 64 except that lime is substituted for whiting. A marked improvement is apparent. The value of the saponified oil is indicated by the

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[13] It was "found by experiment that 3 parts of quicklime to 1 of common salt applied as a wash on brick walls, even when laid on with a syringe, stood remarkably well for four years, and was an efficient and durable coating." Newman, "Metallic Structures. Corrosion and Fouling and Their Prevention," **1896**, Spon & Chamberlain, New York.

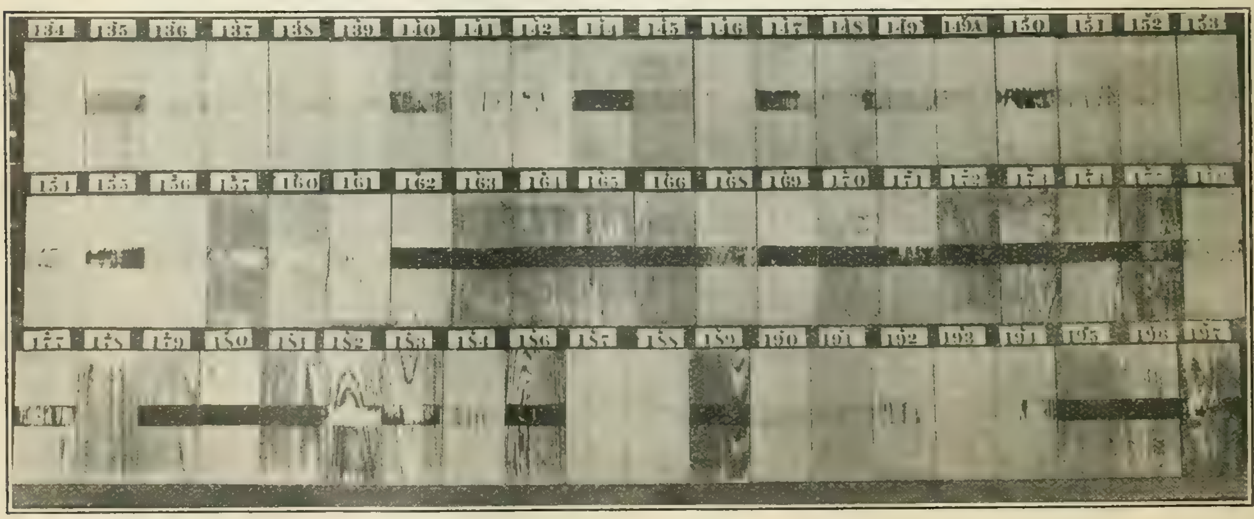

Fig. 5—Appearance of Films after 6-Wk. Exposure. Series 2

TYPE No	FORMULA PARTS PER 50 PARTS OF HYDRATED LIME	WORKABILITY	CHARACTER OF ORIGINAL FILM				DURABILITY,-CONDITION AFTER EXPOSURE			
			APPEARANCE AND CONDITION	INDEX OF ORIGINAL HIDING POWER	WHITENESS INDEX OF CONTRAST WITH		SIX WEEKS		THREE MONTHS	
					BLACK	WHITE	INDEX OF CONTRAST WITH WOOD	APPEARANCE AND CONDITION OF FILM	INDEX OF CONTRAST WITH WOOD	APPEARANCE AND CONDITION OF FILM
134	Casein 5, Na_3PO_4 3	Good Sets rather rapidly	White, hard, enamel-like No chalking	0 (f)	88 (g)	0 (f)	10 (f)	Worn slightly No checks	36 (f)	Worn in one spot otherwise good
135	" 5, " 2	" " "	Trace yellow Hard Enamel like No chalking	14	70	14	15	Good	42	" " " "
136	" 10, " 6, Whiting 25	Better than 134 or 135	" " " "	4	60	4	12	"	16	White, good, No checks
137	" 10, " 6, " 25, HCHO 5	" " 136	Very white Hard, enamel-like, No chalking	0	92	0	10	"	20	Worn slightly, no checks, white
138	" 10, " 4, " 25, " 5	Same as 137	" " " "	0	92	0	15	"	22	" " " " "
139	" 10, " 6	" " "	yellow (b) Hard, enamel-like No chalking	4	70	6	21	Checked slightly	20	Checked Slightly
140 (a)	" 5, " 2, Resin 4 in Oil 12	Good	Yellow Fairly soft rubs slightly	24	60	20	80	Scaled	88	Scaled badly
141	" 5, " 3, $Na_2C_2O_4$ 1	Same as 134	Same as 135	6	76	10	50	"	55	" "
142	" 5, " 3, Na_2F_2 2	Good Sets rather rapidly	Same as 139	0	76	5	42	"	61	" "
144	" 5, " 3, NaCl 15	Fair NaCl ppts Casein	Soft, White NaCl destoys Enamel-like effect	10	80	0	70	" badly	94	Badly worn + scaled
145	" 5, " 3, $ZnCl_2$ 2	$ZnCl_2$ causes precipitation Mixture must be ground	Same as 144	18	80	0	40	Badly worn No checks	60	" " . No checks
146	" 5, " 3, Na_3AsO_4 1	Same as 134	Same as 134	0	70	6	25	Checked slightly	54	Scaled slightly
147	" 5, " 3, Sod Salicylate 1	Good. Salicylate lowers viscosity	Very yellow. Hard, enamel like No chalking	14	60	24	25	" "	79	Scaled badly Wood pigmented
148	" 5, " 1, " 1	Same as 147	Same as 147	10	76	16	50	Checked slightly + Worn	78	" " " "
149	" 6, " 3, ZnO 10	Best of all tried	Trace yellow Good	6	80	8	30	" "	40	Checked slightly Appearance Good
149a	" 6, " 3, " 10, HCHO 5	Same as 149	Same as 134	0	84	0	10	" "	60	Worn. Checked slightly
150	" 5, Silicate 5, HCHO 5	Good	Fair Trace yellow. Hard, enamel like	0	88	3	35	" "	61	Scaled slightly
151	" 5, Na_3PO_4 1, Borax 2	"	Good Trace yellow Hard, enamel like	10	76	6	34	" "	32	Very slightly checked
152	" 5, NH_3 3	Good Better than phosphate mixs	Same as 151	14	68	6	15	Good Worn slightly	16	Good Worn slightly
153	" 5, " 3, HCHO 5	Slightly better than 152	Good Very white Very hard No chalking	8	76	0	16	" " "	17	" " "
154	" 5, " 15, Soap 5, ZnO 10	Good	Good Same as 153	10	72	0	16	" "	60	Badly worn Thin
155	" 5, Na_2CO_3 1	Fair Sets rather rapidly	Same as 153	4	76	0	10	Good	16	Good checked very slightly
156	" 5, Borax 2	Good Casein dissolves slowly	Trace yellow Hard, no chalking	0	72	4	10	"	18	" " "
157	R Oil 12 (c), ZnO 10, HCHO 5	Fair Sets rapidly	White Soft Rubs slightly	4	60	4	97	Almost all off Pigmented	(E)	All off
160	R Tung 12, $ZnCl_2$ 1	Better than linseed mixs Fair	White Med hard, Chalks very slightly	14	70	10	91	Worn and scaled	130	About half off Worn and Scaled
161	Glue 5, HCHO 5	Fair	Trace yellow Med hard, no chalking	24	72	4	56	Worn along edges of grain	80	Worn along edges of grain
162	" 3, " 2	Good	White Med hard, no chalking	14	76	0	64	" " " " "	88	" " " "
163	" 1, Agar Agar 2	Poor Sets too quickly	" " "	0	76	0	(E)	Over half off	(E)	All off
164	" 1, " " 2, HCHO 2	" " "	" " "	12	76	0	(E)	" " "	(E)	" " Wood pigmented
165	" 1, Gum Arabic 2	Good Better than 162	Not perfectly white Med hard No chalking	36	60	10	108	Worn along edges of grain	(E)	" "
166	" 1, " " 2, HCHO 2	Same as 165	Same as 165	16	72	4	95	" " " " "	(E)	" "
168	" 3, Na_3PO_4 5, HCHO 5	Good	Very white. Hard, no chalking	10	72	0	20	Slight Scaling	90	Scaled Discolored slightly
169	" 3, NH_3 3	Good Sets less rapidly	White, hard, no chalking	0	80	4	25	Few checks. Otherwise Good	68	Worn and scaled slightly
170	" 3, $ZnCl_2$ 2	Good	" " " "	0	80	2	83	Worn along edges of grain	(E)	Over half off wood pigmented
171	" 3, Sod Salicylate 1	"	Trace yellow. " "	0	76	6	63	" " " " "	80	Worn along edges of grain
172 (d)	" 1, Whiting ½, Flour 3, NaCl 15	Fair Granulates slightly	" " " "	14	70	3	(E)	Half off, pigmented	(E)	All off
173	" 1, " ½, Flour 3, NaCl 15, HCHO 5	" "	" " " "	4	76	3	128	About half off.	(E)	" "
174	NaCl 1.6, Flour 1.6	" "	" " " "	8	76	3	98	Scaled + worn along edges of grain	125	About half off
175	Flour 5, HCHO 5	" "	Fair Med hard Rubs slightly	8	76	0	(E)	Over half off	(E)	All off
176	Glue 3, Kerosene 10	Fair	White " " " "	0	80	4	70	Worn but quite white	91	Badly worn
177	" 3, NaCl 20	Same as glue-lime mixs	Fair " " " "	18	76	0	88	" " " "	110	" "
178	" 3, " 5	Same as 177	" " " " "	12	80	0	106	Largely worn off	(E)	All off Wood pigmented
179	" 3, " 15, Kerosene 10	" " "	" " " " "	0	80	0	115	" " "	(E)	" " " "
180	" 3, Alum 1	Excellent	White, hard, no chalking	4	40	0	74	Worn along edges of grain	(E)	Worn Over half off
181	" 3, $CaCl_2$ 5	Same as 177	" " " "	14	80	0	118	About half off Pigmented	(E)	" " " "
182	$CaCl_2$ 8	Much better than lime alone	Very white " " "	4	80	0	128	" " " "	(E)	Worn + scaled Over half off
183	" 3	Same as 182	" " " "	8	76	0	107	Worn along edges of grain	130	" About half off
184	Casein 5, $NaHCO_3$ 4.7	Same as Na_2CO_3 mixtures	Trace yellow " " "	0	88	4	60	Edges of grain just showing	85	Worn along edges of grain
186	Hydrated lime alone	Fair	Very white Soft, Chalks	8	84	0	120	About half off	130	About half off

(a). Resin dissolved in boiled oil. All such mixtures remain soft
(b) A number of films, notably those containing Na_2CO_3 are slightly yellow when painted, but this yellowness disappears within a day or two after exposure
(c). Raw linseed oil
(d) Lighthouse formula
(e) No figures are given if film is over half off
(f) Smaller values indicate better films
(g). Larger values indicate better films

TABLE II—TYPICAL FORMULAS. SERIES 2. FIGS. 4, 5 AND 6

final condition of 64*a* as compared with corresponding formulas containing no oil. Number 66 is an old formula in which the scaling may be the combined effect of the silicate and whiting. It is clearly demonstrated in this series that

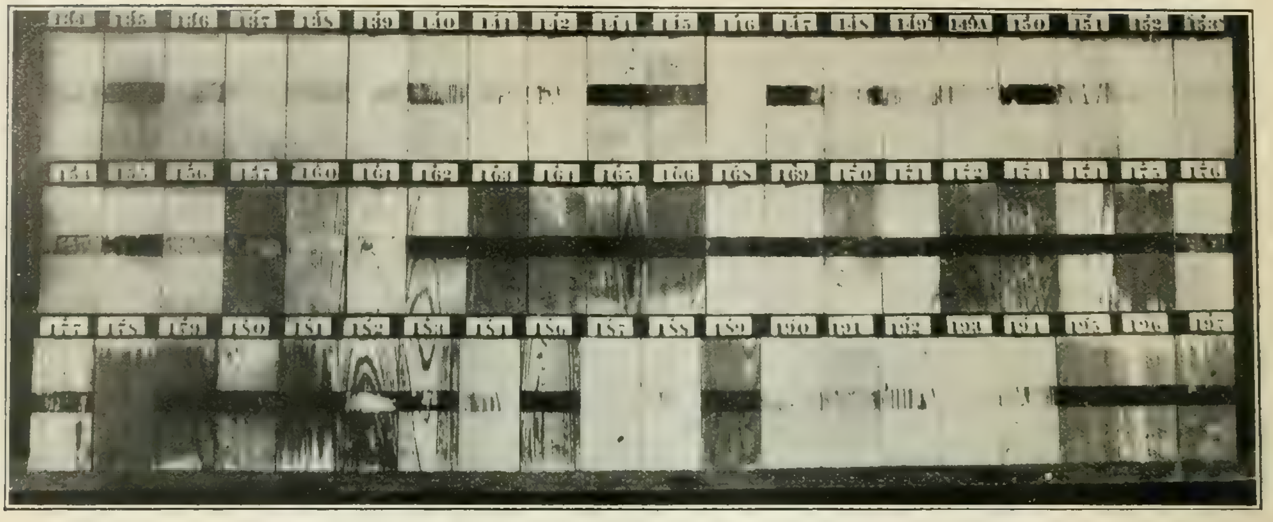

Fig. 6—Appearance of Films after 3-Mo. Exposure. Series 2

formaldehyde improves the workability and durability of glue mixtures.[14]

Numbers 67 to 71 all contain sodium silicate. This substance, either alone or in combination, has no pronounced beneficial effect on a lime whitewash. Preliminary tests indicate, however, that when painted over a dry lime film it may serve as a valuable protective coating.[15] The addition of portland cement to lime washes increases their permanency slightly, as shown by 72. Formulas 74 to 76 contain kaolin, which produces no beneficial effect under the conditions used. Series 77 to 84 have whiting as a common constituent. They are no better and in a few instances not quite so good as the corresponding mixtures in which lime alone functions as the pigment. Whiting improves the workability of most mixtures to some extent, but as a rule decreases hiding power and durability.

Formulas 85 to 87*a* stand out very prominently as among the best. They have lime, whiting, and casein as common constituents. Number 87*a* proved to be the most permanent of Series 1. This formula produces a very hard, white, enamel-like film which was not noticeably changed after a 3-mo. exposure, and after having been subjected 6 mo. to this very severe test had deteriorated only very slightly. It can be washed with soap and water repeatedly without effect, indicating its suitability for interior.

The value of soap in whitewashes is negligible, as is shown by Blocks 88 to 93, except of course where it is required as an emulsifying agent. The negligible effect of rice flour for exterior use is shown by 94 to 102. The improvement of flour formulas by addition of sodium phosphate is indicated by 98. In combination with flour a zinc oxide-zinc chloride mixture seems to have positive value. That an ordinary whitewash is very greatly improved by either magnesium or calcium chloride is conclusively shown by 104 and 105. That the practice of using a small percentage zinc oxide[16] or zinc chloride with lime is justified by results is shown by 107 and 108. Zinc sulfate, however, does not have the same effect (109).

Formulas 110 to 113 contain, consecutively, sodium carbonate, borax, and sodium phosphate combined with lime. These alone do not improve the durability. Kerosene (114) has little or no effect, and alum (116) has slightly less effect than salt. Numbers 117 to 126 contain, in order, silica, plaster of Paris, glycerol, asbestine, copperas, linseed oil and turpentine with no water, sodium fluoride, and glucose in combination with lime alone. Of these, glycerol (119) is the only one of most positive value. Number 122 shows excellent durability but is unsatisfactory because of its transparency and slow drying.

Formulas 127 to 130 are commercial paint preparations bought in the dry form from local dealers. The first three are glue-whiting mixtures; 130 is a lime-casein preparation. This one maintained its equality with 87*a* through the 3-mo. period, but at the end of 6 mo. was almost entirely disintegrated, whereas 87*a* was yet in good condition.

SECOND SERIES—In Table II are listed part of the formulas exposed in the second series. Typical formulas exposed in the first series were duplicated, and certain modifications of these were also tried in an endeavor to produce increased permanence. Fig. 4 shows their appearance when exposed (November 23, 1921), and Figs. 5 and 6, respectively, their condition 7 wks. and 3 mo. later. Unfortunately they did not appear so white after exposure, owing to a discoloration of soot from a nearby chimney. Numbers 186 to 196 are duplicates, consecutively, of Formulas 1, 29, 33, 42, 56, 64*a*, 85, 87, 87*a*, 98, and 119 of the first series, and, with one exception as mentioned above (33), gave results duplicating those of the first test. These formulas are not listed again in Table II.

Numbers 134 to 140 are modifications of the better phosphate-casein formulas of the first series, such as slight variation in the proportions of phosphate or casein or methods of using the formaldehyde, as indicated in the table. No improvement worth mentioning was obtained by these modifications, nor does the addition of sodium oxalate (141) or sodium fluoride (142)[17] improve them. Formulas 144 to 151 are casein mixtures modified by addition of the salts indicated. Salt proves to be incompatible with casein, tending to precipitate it, destroys the enamel or varnish-like effect of the film, and decreases durability. The same is true of zinc chloride and as well of most salts having no alkaline reaction.[18] Sodium arsenate has no appreciable effect, while sodium salicylate improves the fluidity and workability but does not affect the permanence. Zinc oxide improves quite markedly the workability and enhances the whiteness to some extent, but has little effect on the resistance to weathering. The mixture of borax and phosphate is no improvement over phosphate alone. Numbers 152 and 153 proved to be quite satisfactory formulas, being equal to 29 or 87*a* in permanence and slightly better in workability, the ammonia-casein solution being slightly more fluid than that obtained with phosphate. The effect of formaldehyde in this mixture is noticeable only in its slight improvement in workability. Other modifications of original formulas illustrated by 154 to 160 show no improvements.

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[14] See 161 and 162, second series.

[15] Private communications, and results by the writer.

[16] Ordinary lime whitewash may be made better and whiter by adding zinc oxide. Scott, *Loc. cit.*, 225

[17] Brit. Patent 150,555 (1919) describes a paint in which fluorine compounds, such as sodium fluoride, are used. Fourniss, *Papers of the Paint and Varnish Society London*, **1909–10**, mentions the use of a coating of hydrofluoric acid for waterproofing albuminous lime paints.

[18] Scott, *Loc. cit.*, 459.

Of the variations of the glue preparations, 161 to 171 and 176 to 181, Formulas 161, 162, 168, 169, 171, 176, 177, and 180 are all very decided improvements over those of the first series. It is quite evident that formaldehyde, phosphate, ammonia, sodium salicylate, kerosene, salt, and alum each make the paint more resistant, the glue-phosphate and glue-ammonia mixtures being especially durable. The effect of alum on the permanence is not so marked, but it does considerably improve the working qualities of the mixture. The lighthouse formula is repeated as 172 and with the addition of formaldehyde as 173, with a substantiation of the earlier results. Formaldehyde improves this formula, but not sufficiently to justify its use in this combination. The results of variations in quantities of calcium chloride (182 and 183) indicate that the proportions used in 105 were close to the optimum.

In general it may be said that whitewash formulas containing a definite siccative are very much more permanent than those without such an ingredient, and that for exterior use casein and linseed oil are the best binders tried. Those which are water-soluble, such as glue, are not so good for exteriors. The addition of substances, such as formaldehyde, which harden or render the film less soluble, improve considerably the resistance of most films. Of the alkaline salts used for accelerating the solution of casein, trisodium phosphate proved to be the best, its advantage probably depending upon its mild alkalinity. Ammonia also proved to be a satisfactory substance for this purpose. Of the addition agents used with lime in the absence of siccatives, common salt proved to be somewhat more effective than the others.

Tests of the best formulas described above by painting them on stones showed they were as permanent on the stone as on wood and that the order of merit was the same under both conditions. It is planned to extend the investigations to include tests of other formulas and of the same formulas on other materials, such as plaster, brick, and metal. The development of formulas for use on interiors will also be undertaken.

The Manufacture of Reflecting Telescope Disks[1]

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Reflecting telescope disks may be made by casting glass into a suitable mold and annealing. The annealing schedules of Adams and Williamson have been found to be satisfactory. Electric or gas-fired furnaces may be used for obtaining the uniform temperatures necessary, but the gas furnace has been found to be the more reliable. Special equipment is required for obtaining accurate cooling rates, and the Leeds and Northrup electrical control and Robertshaw gas regulator are suitable when slightly modified. If reflector disks are made of low expansion glass the change of figure in a parabolic mirror due to change of temperature can be minimized.

In the past Europe has been the only source of large telescope disks. Recently, however, several large disks have been made in the United States. Reflecting telescope disks have been made by the casting method, but refractor disks are made by molding, for experience has not yet shown whether or not poured disks can be obtained free enough from striae to permit their use for refractors. Moreover, although sufficiently large blocks of homogeneous glass have been obtainable in this country, the principal difficulty in making refractor disks has been the lack of facilities for proper annealing. Although the theoretical requirements for annealing glass to any degree of freedom from strain were understood in the United States, their practical application was not attained until recently because the literature is devoid of reference to the methods and apparatus employed abroad in the manufacture of telescope disks. It had been supposed in this country that gas furnaces could not be used for the careful heat treatment necessary in the annealing of large disks; consequently, an electric furnace was designed by an American manufacturer for this purpose. This furnace, as redesigned by the authors, has proved a success. However, results have demonstrated that a gas-fired furnace is fully as satisfactory as the electric furnace, and is simpler to control. Both furnaces are described in this paper.

The procedure to be outlined here is that actually used in the manufacture of 40-in. reflector disks. Briefly, it consists of pouring molten glass from the pot into a mold, and annealing the glass by means of a specially equipped furnace. This method was devised because the pressing process, although possible for disks up to about 12 in. in diameter, is obviously impossible for those 40 in. in diameter. The annealing treatment discussed herein with reference to reflector disks is applicable also to refractor disks, the manufacture of which will be treated in a subsequent paper.

For casting glass, in addition to the ordinary equipment used in an optical glass factory, apparatus for raising and tipping a pot of glass is required. The contrivances used for pouring plate glass would be ideal, but in their absence the desired results were obtained by employing a bail attached to a chain fall. The pot was held by an adjustable wrought iron ring suspended from the bail. On opposite sides of the ring, short square rods projected through the eyes of the bail. Handles, six feet in length and terminating in a cross bar, were fitted to the square rods, and provided a means for tipping the pot. Except in its simplicity, the equipment differed little from that used in casting plate glass.

The mold into which the glass is to be poured should permit the disk when finished to be easily removed, and must be so made that the glass will not adhere. These requirements were met by a mold of ordinary split firebrick (9 in. × 4.5 in. × 1.25 in.). The bottom of the mold consisted of a heavy iron casting on which the brick were laid.

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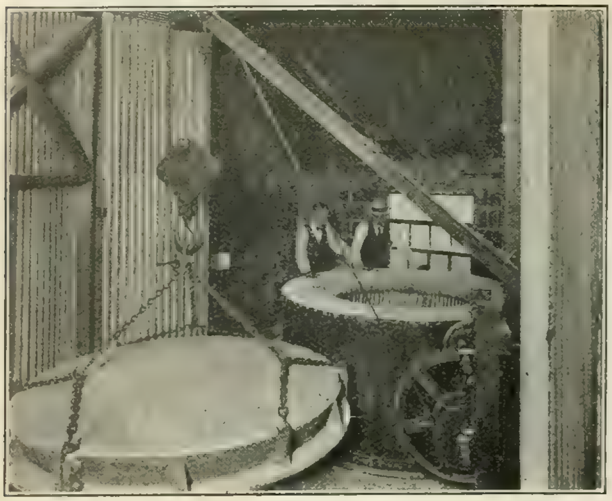
[1] Received March 3, 1922.

The wall consisted of brick laid inside an iron ring or hoop. The iron casting served not only as a support for the mold, but also as a means of obtaining uniformity of temperature. A layer of talc over the lining of the mold prevented the glass from adhering.



[Fig 1—Electric Furnace as Originally Constructed. Rheostat and Leeds and Northrup Controller in Background at Left

In order to insure the uniform temperature conditions that are necessary for good annealing, a cast-iron cylinder of the same diameter as the heavy plate mentioned above was employed. The cylinder, together with a cover of the same size as the bottom plate, made it possible, after the disk was poured, to encase the whole mold in iron. The higher thermal conductivity of the metal casing as compared to that of the brick and glass minimized temperature inequalities in the disk. Inasmuch as the existence of a temperature gradient during the first part of the annealing results in an unsymmetrical strain in the finished article, it is necessary to take particular pains to obtain uniform temperature conditions.

The annealing schedule for a disk 40 in. in diameter and 8 in. in thickness calls for holding the glass 7 days at a constant temperature, and cooling after the expiration of this time at an initial rate of 0.2° C. per hr. The rate may gradually increase, so that the total annealing time need not greatly exceed 2 wks. Two types of furnace have been successfully employed for this work, an electric furnace controlled by a standard G. E. panel, and equipped with a Leeds and Northrup recorder; and a gas furnace consisting of a slightly altered pot arch provided with a modified Robertshaw temperature regulator. The gas furnace proved as satisfactory as the electric furnace, and had the added advantage that it required a less skilled operator. It should be observed, moreover, that power interruptions may prove a serious disadvantage in the use of an electric furnace.

The Electric Furnace

The heating element of the electric furnace (Fig. 1) originally consisted of a heavy ribbon of nichrome alloy held by porcelain hooks, and wound up and down throughout the interior of the cylindrical furnace lining only. This disposition of the resistance ribbon proved unsatisfactory, as heat was transmitted only to the sides of the charge. Consequently, after several experiments, it was found possible entirely to surround the charge with heat by transferring a part of the resistance ribbon from the side walls to the inside of the bottom and cover of the furnace, in a manner resembling the spokes of a wheel (Fig. 2). To permit the furnace to be opened, the cover was designed as a separate heating element capable of being connected in series with the other element when the furnace was in operation.

The lining of the furnace was of firebrick 4.5 in. in thickness, the inside diameter of the cylinder being 48 in. The insulation surrounding the lining consisted of a 9-in. wall of Sil-O-Cel brick, and the insulation in turn was protected by a heavy iron casing. The bottom of the furnace was of the same material and thickness as the sides. The top consisted of a 9-in. firebrick crown built up on a heavy circular cast-iron ring, and was of necessity movable in order that the furnace might be filled and emptied. A sheet-iron cylinder, covering tightly the outer furnace wall, was placed over the firebrick top. The cylinder was about 24 in. high and was filled with sand or Sil-O-Cel powder in order to insulate the firebrick top.

The temperature of the furnace was controlled by a system of relays operated by the potentiometer recorder, the latter being connected to two Hoskins thermocouples. The thermocouples measured temperatures at two different points: the one, with its junction adjacent to the heating element, recorded fluctuations in temperature of the heating medium supplying heat to the furnace, and the other, with its junction extending into the interior of the furnace where it touched the center of the charge, provided a record of the heat treatment of the disk. By maintaining at the outer thermocouple a certain temperature, which incidentally may fluctuate more or less to either side of the desired degree, a remarkably steady temperature, slightly lower than that at the resistance element, was sustained in the furnace. The proper temperature was maintained by means of the control mechanism of the recorder.

Two fiber disks, A and B, about 6 in. in diameter, were mounted behind the recording instrument; these disks were so arranged as to rotate with the potentiometer slide wire, and, accordingly, any movement from the zero of the potentiometer was followed by a similar movement of the fiber control disks. On the edges of each control disk were mounted two brass strip contacts, and a stationary finger fixed to the frame of the instrument made contact with the brass strips of each disk. An additional contact point, which was adjustable, also made contact with the strips on disk B.

These disks and fingers play an important part in the operation of the furnace, for by making and breaking the proper circuits, relays are operated which throw the current on and off the furnace. Of the three contact fingers, one serves to determine the maximum temperature to which the resistor will be allowed to rise, another serves to operate

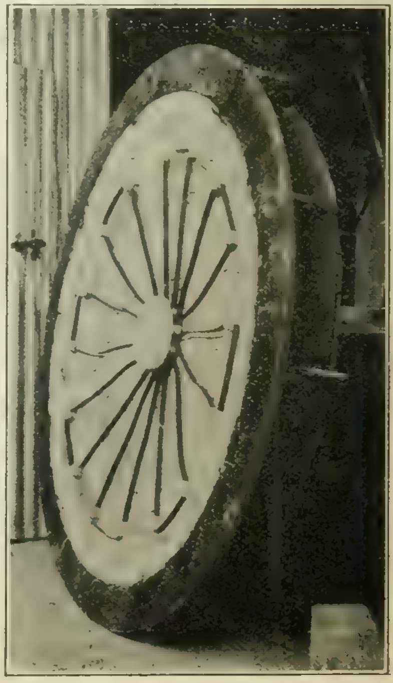


Fig. 2—Furnace Cover after Rewiring

the closing relay whenever the charge cools off below its scheduled temperature, and the third, or the adjustable finger, serves to make and break the circuit between certain limits, thereby holding the resistance element at the proper temperature above that scheduled for the disk. In order to maintain the proper temperature in the charge, it is necessary, before setting the adjustable finger, to determine the temperature difference between the charge and the ribbon. The control for determining the maximum temperature of the ribbon is desirable, in order that the loss by radiation may be supplied from a source only slightly higher in temperature than that of the charge; but for the rapid heating of cold molds, and in order not to lose time, it is desirable to heat the ribbon to a high temperature.

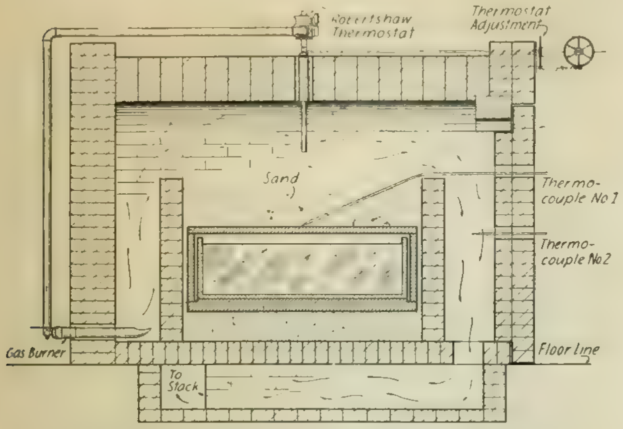


Fig. 3—Cross Section through Center of Gas Furnace, Showing Location of Disk Thermocouples, Regulator, Etc.

In addition to the automatic controller, a large adjustable rheostat was used, capable of reducing the furnace input from its maximum of 24 kw. to about 5 kw. The use of the rheostat permitted greater flexibility in the operation of the automatic control, for when the input was cut down by the rheostat to a degree that maintained the furnace temperature a little hotter than the required schedule, the "make and break" in the relay system became less frequent.

The apparatus described above served very well to hold the furnace at a definite temperature, but for cooling the furnace at a predetermined rate, adjustments had to be made by hand. For cooling with comparative speed, it was possible either to utilize the rheostat, or repeatedly to set the adjustable contact finger of the recorder mechanism, or to use both. However, for very slow cooling rates it was necessary to rely upon the automatic mechanism alone, and by regular adjustments obtain the average cooling rate required. These adjustments required, by reason of their frequency and nicety, the constant attention of a skilful operator, and to obviate this burden an automatic device was developed. This device was merely an adjustable backgearing mechanism for altering the setting of the adjustable finger, and, in conjunction with the apparatus described above, provided any desired cooling rate from 0.2° C. per hr. to 1° C. per hr. Higher cooling rates could be obtained by the use of the rheostat. As previously stated, the electric furnace was not as satisfactory as the gas furnace.

The Gas Furnace

The gas furnace (Fig. 3) consisted of a regular pot-arch enlarged to accommodate the iron cylinder and mold. The fuel used was natural gas burned behind a breast wall by means of three burners of the Bunsen type. A small track was laid down on the floor of the pot-arch, and a short movable section of track was so arranged outside as to permit a strong car to be rolled in and out of the furnace. The car served as a carriage for the mold. The auxiliary section of the track was so made that it could be moved about on a transveyor truck. The temperature of the furnace was controlled by a special Robertshaw regulator.

The Robertshaw regulator (Fig. 4) consists of a valve actuated by the differential expansion and contraction between a carbon rod and a copper tube. In this installation, the expansion tube extended through the crown and into the interior of the furnace about 8 in. A worm gear and handle served for adjusting the regulator valve and for determining the temperature. The device has an arbitrary scale, and its calibration must be determined for each installation.

The Casting Process

The glass was melted and fined in accordance with the 24-hr. process,[2] which has been so fully treated in the literature as to require no discussion here. While the glass was being melted, the mold was heated in an auxiliary furnace for a period of 5 hrs. at 100° C., and was then raised to about 500° C., by which treatment the moisture was entirely removed from the mold. This point was reached, and the mold removed from the furnace, several hours before the former was required for further process.

The glass was cooled in the usual manner, and when the melt reached the proper temperature the stirring machinery was taken away. The pot was at once removed from the furnace on a pot carriage and placed upon clay blocks immediately beneath the crane. The hoisting apparatus was adjusted, a cover of heavy asbestos board placed on top of the pot, and the melt permitted to chill for several minutes.

The manner and extent of cooling are important, for if the glass is too hot when poured, bubbles will form when it strikes the mold; and, on the other hand, if poured too cold, the glass flows slowly, and by layering entraps air. In fact a successful pouring depends to a very great extent upon the decision and skill with which the operation is performed. In this connection, it is to be noted that a measurement of the actual temperature of the glass is difficult because of the apparent opacity of the surface of the glass to the radiation of the hotter glass beneath. A relative measurement is unsatisfactory, affording no means of control by reason of the practical impossibility of exactly duplicating conditions. Accordingly, the exact temperature at which the pouring should be made has not been determined, although the moment for pouring was successfully ascertained in each case by an experienced workman, who determined the proper viscosity by applying an iron rod to the surface of the glass. Further experimentation will undoubtedly establish a method for determining, in a more

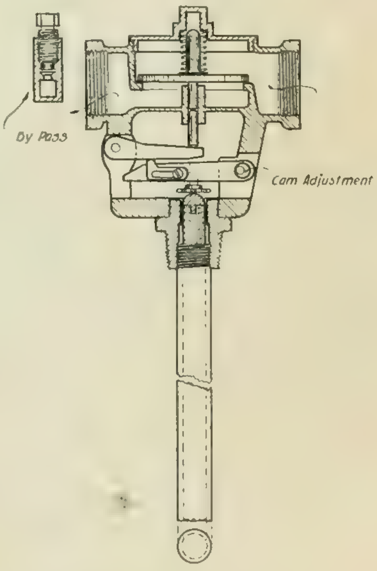


Fig. 4—Cross Section through Center of Robertshaw Temperature Regulator

accurate and satisfactory manner, the exact temperature at which to pour.

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[2] G. W. Morey, *J. Am. Ceram. Soc.*, **2** (1919), 146.

The proper moment for casting having arrived, the mold was placed close to the pot, which was raised and slowly tipped through an angle of about 120° (Fig. 5). The relative positions of the mold and the pot were then carefully adjusted so the molten glass struck the mold at its very center and slowly, and without folding, filled out the mold to its edges. When sufficient glass was poured, the pot was so quickly tipped back to and beyond its original position that the rapidly diminishing stream of glass was caught upon the side of the pot, thereby greatly minimizing the number of bubbles formed from folds in the surface of the glass.

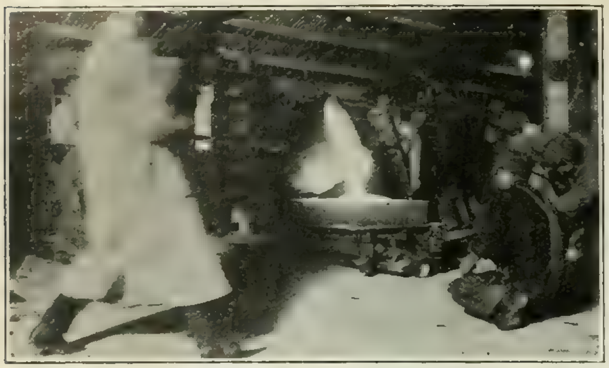

FIG. 5—CASTING A REFLECTOR DISK

When the disk was annealed in the electric furnace the mold was immediately transferred to the furnace, where it was carefully raised and lowered into the interior. The cast-iron cylinder and cover were then hoisted into place, as was also the heavy furnace cover after the thermocouples had been placed in their proper position. When the gas furnace was employed, the cast-iron cylinder and cover were immediately put into place, the transveyor truck moved to its position at the front of the pot-arch, and the mold carriage rolled in on its track. A wall of brick and clay was quickly built up in front of the disk, and the furnace filled with sand to a depth over the mold casing of approximately 6 in., leaving a space, however, of about a foot beneath the crown for the passage of heat from the burners. Thus the disk inside the casing was insulated with sand on all sides. Two thermocouples were arranged, the one with its hot junction in contact with the center of the iron plate above the disk, and the other projecting a few inches inside the door of the furnace. The fire was at once turned on full until the temperature of the furnace was from 50° to 100° C. above that of the disk, and was then gradually lowered until the disk reached its annealing temperature.

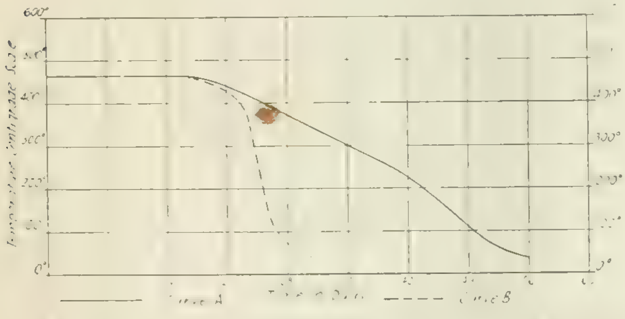

FIG. 6—CURVE B, THEORETICAL SCHEDULE FOR ANNEALING A SLAB 8 IN. IN THICKNESS
CURVE A, SCHEDULE ACTUALLY USED ON 40-IN. DISKS

The annealing schedule actually used on 40-in. disks was longer than was necessary. According to the work of Adams and Williamson,[3] a slab of borosilicate glass 20 cm. thick should be suitably annealed if held for 7 days at the proper annealing temperature, and then cooled according to the following schedule:

RATE	° C. per Hr.
Initial	0.2
After 10°	0.3
After 20°	0.4
After 30°	0.5
After 40°	0.6
After 50°	0.8
After 60°	1.1
After 70°	1.5
After 80°	2.0
After 90°	2.8
After 100°	4.0

Maximum cooling rate 6° C. per hr.

The annealing temperature used was determined from a sample taken from a previous melting. To allow for a sufficient factor of safety, the disk was held at its annealing temperature for 14 days, a period twice as long as was necessary. This temperature for glass 8 in. in thickness was 464° C. Cooling followed in accordance with the schedule of Adams and Williamson as outlined above, although the maximum cooling rate was retarded so as not greatly to exceed 1° C. per hr., a precaution doubtless unnecessary. However, below a temperature of 100° C. it would be difficult to cool the furnace at a more rapid rate; rapid cooling accelerated, for example, by opening the furnace door, must be avoided by reason of the probability of uneven cooling setting up dangerous temporary strain. Theoretically, to be sure, the tensile strength of the glass should permit a disk to be cooled toward the last at a rate even in excess of 6° C. per hr., and such a rate would permit a very appreciable and important saving of time; but practically its use invites disaster, and it was, therefore, deemed advisable to employ a slower, and, consequently, a safer cooling rate. A comparison of the two curves shown in Fig. 6 will show the time which might possibly be saved by using the theoretical schedule.

It is unnecessary to state that the ease with which the schedules were maintained resulted from the automatic controlling devices. For example, when operating the electric furnace, the temperature of the ribbon, and consequently of the furnace and its charge, was determined by the setting of the recorder, for when the temperature of the ribbon reached the maximum limit as set by the recorder, the current was automatically broken, and then, as the temperature of the ribbon lowered and reached the minimum set by the recorder, the automatic control operated to complete the circuit. The difference in temperature between the maximum and minimum limits was constant, corresponding to the distance between the two brass strip contacts mounted on the fiber disk B. By this means, just enough heat was added to supply that lost by the furnace and disk, and a remarkably constant temperature was thereby maintained in the latter. By lowering the setting of the instrument the two limits were lowered equally, and consequently the temperatures of the ribbon, furnace, and disk lowered accordingly. Throughout the upper range both limits were set above the temperature of the disk, and in the lower range gradually approached its temperature until at about 75° C. all temperatures practically coincided. At this point, the free cooling rate of the furnace became less than was required by the schedule, so the power was shut off.

Control of the gas furnace followed somewhat different lines. In the gas furnace heat was supplied continuously, and the temperature of the furnace was held constant by the thermostatic regulator, which, at the slightest cooling, opened to admit more gas, and *vice versa*. Owing to the insulation of sand, considerable lag existed between the temperature of the furnace and that of the disk, and consequently, slight changes in the temperature of the former did not affect the disk. In order to maintain the desired temperature in the disk, it was necessary to operate the furnace at a higher temperature. The difference varied with each run, but averaged about 100° C. at the annealing temperature, and gradually decreased as the disk was cooled.

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[3] *J. Franklin Inst.*, **190** (1920), 850.

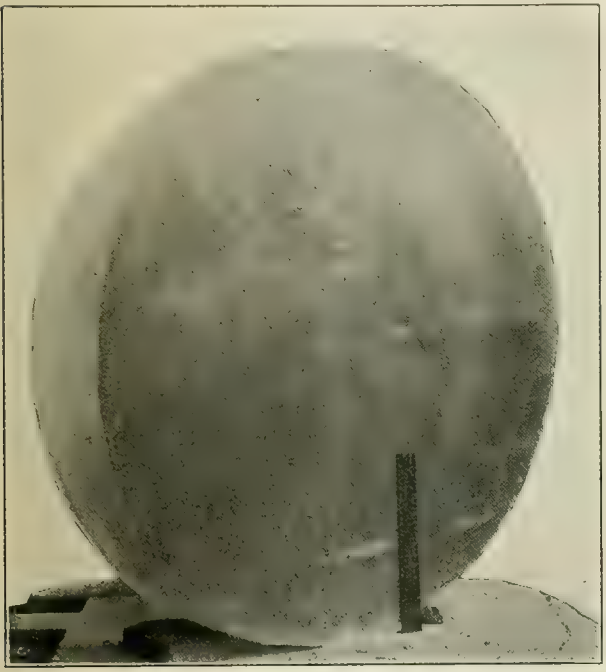

Fig. 7—A 40-In. Telescope Disk Standing on Edge
(The ruler is a 12-in. one)

A few observations on the general utility of the regulating devices may be of interest. In operating the electrical equipment it was merely necessary to check against the standard cell each day, roll up the record paper, and inspect the machine. The pen required filling every two or three days. The chief source of trouble in this control is the possibility of an arc forming on one of the intermittently operating contact points, which may not only cause erratic operation of the relays, but may fuse the contacts and thereby impair the functions of the controller. In one instance, an arc formed on one of the control disks at the point where the contact slider changes from the "current on" side to the "current off" side. This carbonized the fiber of the insulating disk, and short circuiting the two sides, caused the opening and closing coils to operate simultaneously.

The gas regulator may be expected to give little trouble, although care must be exercised that the expansion tube be tightly fastened to the valve mechanism, for should it become loosened a drop in temperature will result. Also, the valve must be properly set before the run is commenced, so the desired range of temperature control is within the range of the instrument, for otherwise, as adjustments are subsequently made to cool the furnace, a point will be reached where further adjustment will increase rather than diminish the temperature. This is due to the cam adjustment which has no minimum stop.

Advantage of Using a Low Expansion Glass

It is a fact quite generally accepted that, where a telescope disk is to be used as a reflector, the optical properties of the glass used are of no particular importance, and that from this standpoint it is, therefore, possible to employ any type of glass possessing good weathering qualities, such as, for example, the commonly used crown glass. However, the use of ordinary crown glass is a contributing factor to a well-known difficulty encountered in the use of reflecting telescopes, namely, the effect of temperature changes.

Astronomers using reflecting telescopes are familiar with the effects caused by changes of temperature in parabolic mirrors, as, for example, when the mirror is exposed to radiation and becomes heated, the glass expands, and the shape of its surface changes. It is to minimize the effect of changes in temperature, convection currents, etc., that parabolic mirrors are usually protected by an insulating chamber. Furthermore, it is an accepted experience that when these undesirable surface changes occur, the resultant effect on the definition of the reflector is, on the average, toward under-correction. It has accordingly been suggested that this difficulty might be minimized provided the parabolic mirrors were made with a slight degree of over-correction.[4] Obviously, however, it is preferable to eliminate entirely the cause of the under-correction, and this desideratum was kept in mind in determining the composition of the glass to be used.

The glass used for casting the disks mentioned herein was a borosilicate glass of the following composition:

SiO_2	70.8
K_2O	14.4
Na_2O	5.4
CaO	2.0
B_2O_3	7.2
As_2O_3	0.2
	100.0

Its selection was based on the fact of its lower expansibility than that of ordinary crown glass, for it is clearly established that a change of figure in a parabolic mirror during changes of temperature depends primarily on its expansibility. Ordinary crown glass has a coefficient of expansion of about 0.000011 per ° C., but stable glasses can be made with expansion coefficients anywhere from 0.000003 up to and beyond the expansion of ordinary crown glass. The glass used had a coefficient of expansion of about 0.000009. However, there is no great difficulty in making disks of glass with a still lower expansion coefficient. It should nevertheless be noted that as the expansion coefficient is reduced, it becomes increasingly difficult to eliminate from the glass small bubbles, which seriously interfere with the formation of a satisfactory mirror surface.

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[4] J. S. Plaskett, *J. Roy. Astronom. Soc. Can.*, **14** (1920), 193.

Centennial of Founding of Hobart College

Hobart College, Geneva, N. Y., is to celebrate the one hundredth anniversary of its founding on June 13, 1922. President Smith has delegated Prof. W. R. Orndorff, of Cornell University, to represent the American Chemical Society at this meeting.

Location List of Chemical Periodicals

The Research Information Service of the National Research Council is compiling a "location list" of chemical periodicals for the use of chemists and librarians. At the present time, the Service has sent out to many of the libraries of the country lists of the chemical periodicals which are abstracted in *Chemical Abstracts*, with the request that periodicals available in the library be checked. When the list is completed, it is to be published. Until this has been done, information can be obtained by applying to C. J. West, Research Information Service, National Research Council, Washington, D. C.

Production of Ammonia by the Sodium Cyanide Method[1,2]

By **F. E. Bartell**

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During the war a study was made of the reactions attendant upon the process of steaming Bucher cyanized briquets. It was found that sodium cyanide and sodium cyanate were readily hydrolyzed, giving theoretical yields of ammonia. The iron present in the briquets caused sodium ferrocyanide formation which introduced certain difficulties.

The formation of ferrocyanide starts at the beginning of the steaming process, and reaches a maximum at the temperature of about 475° C., above which temperature it is decomposed. The rate of decomposition is materially increased with increase in sodium carbonate content. Decomposition of sodium ferrocyanide in the presence of sodium carbonate results in but a slight loss of fixed nitrogen, owing to the formation of cyanide and cyanate, which products are readily hydrolyzed, giving ammonia.

Proper temperature regulation during the process of steaming is highly important. Under a pressure of not over one atmosphere, the limit of pressure in this investigation, the temperature at the beginning of steaming should be about 260° C. and should not be allowed to rise above about 650° C. At higher temperatures ammonia is lost by decomposition.

The rate of steam admission is an important factor. If the steam is added too slowly at first, the temperature will not rise rapidly enough to conform to the conditions that are apparently most favorable. If the steam is added too rapidly, ammonium carbonate is formed with attending difficulties. The quantity of steam added must be sufficient not only to hydrolyze the cyanide and related compounds, but also to oxidize the free iron which is present. In order to insure sufficient steam it seems best to use approximately 50 per cent excess over the theoretical amount.

With 4- and 8-in. batch retorts cyanide conversion to ammonia ran from 85 to 100 per cent. With 10-in. batch retorts (capacity 300 lbs. briquets) ammonia recovery of 99 and 100 per cent was obtained. With 16-in. retorts (capacity 640 lbs. briquets) yields as high as 93.7 per cent were obtained.

A continuous steamer was developed with an estimated capacity of 100 to 200 lbs. of briquets per hour. One run was made with this steamer. The ammonia recovery was 97.8 per cent.

Shortly before the close of this work continuous operations were being carried on. Two cyanizing retorts such as those used at Saltville were put into operation. Each retort was capable of producing from 30 to 50 lbs. of (20 to 30 per cent NaCN) cyanized briquets per hour. Since the briquets were conveyed from the cyanizer directly to the steaming retorts, and after steaming back to the cyanizing retorts, the whole process was continuous. With this layout, coke, nitrogen, and steam were used as raw materials, and ammonia was produced in quantities corresponding to the capacity of a single technical unit.

At the time of the Armistice the results of this investigation had shown that the cyanide process offered a feasible and sure method for the production of ammonia. Its advantage lay in the fact that no electrical power was needed. Its main drawback was the relatively high cost of cyanide production.

SHORTLY after the entry of the United States into the war, three processes for the fixation of atmospheric nitrogen were considered by the War Department as offering practical methods for the production of ammonia and ammonium nitrate.[3] The processes were the synthetic ammonia (Haber) process, the cyanamide process, and the cyanide process. It is well-known history that the Government constructed plants for the manufacture of ammonia by the first two processes. The result of this work has been well covered in recent chemical literature.

In the United States prior to 1917 none of the above ammonia processes had progressed beyond the experimental stage. It was definitely known that ammonia could be produced by the cyanamide process, and further that such a process was in actual operation in Germany with an estimated production for 1917 of 400,000 tons of cyanamide. It was known also that the synthetic process was in apparently successful operation in Germany, though it had never been successfully operated in this country. The cyanide process was to a still greater extent in the experimental stage. Furthermore, on paper, the cost of production of ammonia by the cyanide process appeared to be greater than the cost of production by either of the other processes.

Near the close of the year 1917, the War Department, realizing that cyanide was needed for purposes other than the formation of nitrates, decided to attempt the development of the cyanide process. Late in December 1917 plans were made for the construction of a cyanide plant under the direction of the Bureau of Mines; accordingly a plant was built at Saltville, Va., with a capacity of 10 tons sodium cyanide per day.[4]

At the same time an active research on the production of ammonia from cyanide was undertaken by the Nitrate Division of the Ordnance Department, coöperating with the Nitrogen Products Co., of Providence, R. I., at the experimental plant of this company in Greene, R. I.

In January 1918 this work was placed under the direction of the writer (then Captain, Nitrate Div. Ord. Dept.) and Donald V. Lowe (Lieutenant, Nitrate Div. Ord. Dept.), who were later given the assistance of about thirty men, including chemists, chemical engineers, and assistants. With this group much of the work was carried on in shifts, making it possible to conduct continuous experiments over long-time intervals.

Coöperative research was simultaneously carried on at the Geophysical Laboratory in Washington,[5] and at the U. S. Chemical Plant in Saltville, Va.[6]

The main object of the research at the Greene, R. I., laboratory was the development of a method for the production

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[1] Received February 2, 1922.

[2] This article is printed with the approval of the Chief of the Ordnance, U. S. A., also with the approval of Mr. Edward E. Arnold, President of the Nitrogen Products Co.

The author wishes to express his indebtedness to all the men who so ably and faithfully coöperated in this work and to whom credit is equally due. The men who were most closely associated with the work of this paper are: Mr. Donald V. Lowe (formerly Lieutenant Ord. Dept.), Mr. H. E. Kaiser, Mr. O. E. Madison, and Mr. P. A. Keene; also fullest appreciation should be expressed for the valuable assistance and advice of the officers of the Nitrogen Products Co., particularly to the President, Mr. Edward E. Arnold, whose untiring efforts were largely responsible for the success of this work.

[3] Report of Nitrate Supply Committee, THIS JOURNAL, **9** (1917), 829.

[4] C. O. Brown, THIS JOURNAL, **11** (1919), 1010.

[5] J. B. Ferguson and P. D. V. Manning, *Ibid.*, **11** (1919), 946.

[6] G. W. Heise and H. E. Foote, *Ibid.*, **12** (1920), 331.

of ammonia directly from the cyanide present in the cyanized briquets, such as were to be made by the Bucher process at Saltville. Briefly, it may be stated that the steaming process for conversion of sodium cyanide to ammonia was finally developed in the laboratory at Greene to a point where practically the theoretical yield of ammonia could be obtained by employing batch retorts, and also good yields were obtained with continuous retorts. With 8-in. and 10-in. batch retorts, 100 per cent yields were obtained; with 16-in. batch retorts, with capacity of 600 lbs. of briquets, as high as 93.7 per cent yields were obtained.

During this work it became evident that by far the largest part of the cost of ammonia production by this method was due to the high cost of producing cyanized briquets; consequently, the cyanizing end of the process was also investigated in the Greene laboratory, with the result that yields were finally obtained over comparatively long periods which were considerably higher than any yields previously recorded by this method.

Scope of Work

The work covered in the research carried on at Greene may be classified under three heads:

1—Laboratory research work which had to deal for the most part with equilibrium studies.

2—Small scale work in which both cyanizing and steaming reactions were carried out in retorts from 2 in. to 8 in. in diameter, these retorts having a briquet capacity of from 2 to 40 lbs. of material.

3—Large scale work.

(a) Batch steaming work with retorts 8 in. to 16 in. in diameter with a capacity from 150 to about 600 lbs. of material.

(b) Continuous steaming work, with retorts with a capacity as high as 100 to 200 lbs. of briquet material per hour.

(c) Continuous cyanization work with large-sized units, each capable of handling from 50 to 100 lbs. of briquet material per hour.

(d) Final development of a complete and continuous cyanizing and steaming process.

The Cyanide Process

The cyanide process controlled by the Nitrogen Products Company is the so-called Bucher process[7] in which nitrogen is passed through a heated mixture of coke, soda ash, and iron. The iron is present merely to serve as a catalytic agent. In practice the coke, soda ash, and iron are brought together in the form of briquets. This material is heated in retorts to a temperature of at least 1000° C. Pure nitrogen is passed through the mass which gives the following reaction:

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO - 138{,}500 \text{ cal.} \qquad (1)$$

During this process carbonate is converted into cyanide and the physical properties of the briquets are not seriously altered. In this condition they are well suited to the steaming operations which are later employed to convert the cyanide to ammonia.

Hydrolysis of Cyanide

The hydrolysis of cyanide may be caused to take place in three stages according to the following reactions:

$$2NaCN + 4H_2O = 2NH_3 + 2HCOONa + 64{,}000 \text{ cal.} \qquad (2)$$

This reaction is exothermic and takes place at low temperatures, 100° C. to 200° C. Above 200° C. sodium formate is converted into oxalate:

$$2HCOONa = Na_2C_2O_4 + H_2 - 3{,}000 \text{ cal.} \qquad (3)$$

This reaction is endothermic. At 360° C. this reaction will go to completion. At a still higher temperature, somewhat above 400° C., sodium oxalate is converted into carbonate:

$$Na_2C_2O_4 = Na_2CO_3 + CO - 14{,}800 \text{ cal.} \qquad (4)$$

This reaction is endothermic. The complete reaction may be written:

$$2NaCN + 4H_2O = 2NH_3 + Na_2CO_3 + H_2 + CO + 46{,}200 \text{ cal.} \qquad (5)$$

The total heat effect of the reaction is exothermic.

If sodium cyanide (or cyanized briquets) is treated with saturated steam, Reaction 2 only takes place and sodium formate is the product of reaction. If dry superheated steam is used, the temperature of the mass rises, as a result of the exothermicity of the reaction. If the cyanide content of the briquets is sufficiently high and the thermal conduction from the retort low, the temperature will be raised sufficiently to result in carbonate formation. The advantage of the latter reaction is that when sodium carbonate is formed in steaming, the briquets again contain the materials necessary for cyanide formation and, owing to their dryness, are again in condition for recyanizing. By employing this method it is possible to pass the briquets through the cyanizing-steaming-cyanizing cycle a number of times (at least three or four) without remaking or refortifying them.

Hydrolysis of Cyanate

During the cyanization and subsequent cooling of briquets, some sodium cyanide is oxidized to cyanate; also during steaming some cyanate is formed. The presence of cyanate offers very little difficulty.

$$2NaCNO + 3H_2O = Na_2CO_3 + 2NH_3 + CO_2 + 15{,}340 \text{ cal.} \qquad (6)$$

All of the combined nitrogen in this compound is converted into NH_3. The only difficulty comes through the presence of carbon dioxide, which is liberated and which may react with the ammonia gas to form ammonium carbonate. If the carbonate is formed in comparatively large quantities it may cause trouble by plugging the ammonia scrubber system.

Complication of Steaming Due to Presence of Iron

The presence of iron tends to complicate the reactions which take place during the process of steaming. The principal difficulties encountered are the formation of ferrocyanide and the subsequent reactions of this compound.

Briquets taken directly from the cyanizing retorts and conveyed to the steaming retorts with as little handling as possible adsorbed about 0.2 per cent moisture. If allowed to stand for a number of days they took up a maximum of about 3 per cent moisture. The rate of adsorption is shown in Table I:

Table I

No.	Treatment of Briquets	Water Content Per cent
1	Direct from cyanizer	0.20
2	Exposed 1 hr.	0.72
3	Exposed 3 hrs.	1.80
4	Exposed number of days	3.04
4	Then dried at 250° C	0.42

The above experiments showed clearly that cyanized briquets should not be handled and exposed to the atmosphere for any appreciable length of time before steaming. It was found that briquets which contained as high as 20 per cent cyanide would, at the very beginning of steaming operations, owing to the iron present, have as high as 40 per cent of total cyanide converted into ferrocyanide. The formation of sodium ferrocyanide and hydrate of sodium ferrocyanide causes not only chemical difficulties, as will be shown later, but also mechanical difficulties. If the hydrate of sodium ferrocyanide is formed rapidly in the early stages of steaming, "setting" of briquets and sticking in the retort occur. With continuous retorts this becomes a serious problem. In this connection the principal facts to be kept in mind are:

1—If briquets containing moisture are used, the hydrate of the ferrocyanide will be formed when the briquets are heated to the temperature suited to its formation.

2—If wet steam is allowed to come in contact with heated briquets the ferrocyanide hydrate will form quickly.

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[7] Bucher, This Journal, 9 (1917), 233.

3—If dry steam is allowed to come in contact with briquets which have not been heated above the temperature limit for ferrocyanide hydrate formation, the temperature of the system will be lowered by heat transfer and the hydrate will form.

In order to avoid these difficulties, the briquets must be heated to a temperature above that suited to hydrate formation and, also, superheated steam must be used.

In much of the steaming work, cyanized briquets which had been made in the Saltville, Va., plant of the Nitrogen Products Company were used. These briquets contained from 12 to 17 per cent iron. In some of the later cyanizing experiments it was found that briquets containing much less iron could be used and still give good yields of cyanide. With such briquets the difficulties due to ferrocyanide formation were greatly decreased.

Principal Secondary Reactions

The more important secondary reactions in the steaming process are as follows:

1—As the steaming of briquets proceeds, the iron present is oxidized to the oxides FeO and Fe_3O_4. The latter reaction goes practically to completion at a temperature of about 500°:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2 \qquad (7)$$

2—Iron or the oxides of iron may react with sodium cyanide and steam to form sodium ferrocyanide:

$$6NaCN + Fe + 2H_2O = Na_4Fe(CN)_6 + 2NaOH + H_2 \qquad (8)$$

$$\text{or } 6NaCN + FeO + H_2O = Na_4Fe(CN)_6 + 2NaOH \qquad (9)$$

3—During the process of steaming the ferrocyanide thus formed may be decomposed:

$$Na_4FeC_6N_6 = 4NaCN + Fe + 2C + N_2 \qquad (10)$$

This decomposition is practically complete at a temperature of about 500°. Fixed nitrogen is lost in this reaction.

4—Sodium ferrocyanide may react with other compounds present, such as sodium carbonate or ammonium carbonate. With sodium carbonate the reaction is:

$$Na_4FeC_6N_6 + Na_2CO_3 = 5NaCN + NaCNO + CO_2 + Fe \qquad (11)$$

The nitrogen products of this reaction would be hydrolyzed by steam so no loss of nitrogen would result.

5—In the presence of free iron ammonia is dissociated:

$$2NH_3 = N_2 + 3H_2 \qquad (12)$$

The active decomposition of ammonia begins at about the upper limit of temperature needed for the completion of the steaming reaction. In practice no serious loss of ammonia results from this reaction.

6—A loss of carbon through oxidation by steam results at low temperatures through the reaction:

$$C + 2H_2O = CO_2 + 2H_2 - 41{,}560 \text{ cal.} \qquad (13)$$

and at higher temperatures through the well-known gas reaction:

$$C + H_2O = CO + H_2 - 42{,}330 \text{ cal.} \qquad (14)$$

A large excess of steam should be avoided, since not only is carbon wasted but in addition the system is cooled owing to the endothermicity of the reaction.

These reactions are the principal ones which take place during the process of steaming. Other reactions are possible and other reactions do actually occur, giving compounds not included in the above equations; none of the other reactions, however, have introduced serious difficulties into the process. Ideal reactions for the entire process are as follows:

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO \qquad (15)$$

$$2NaCN + 4H_2O = 2NH_3 + Na_2CO_3 + H_2 + CO \qquad (16)$$

$$\text{or } 4C + N_2 + 4H_2O = 2NH_3 + H_2 + 4CO \qquad (17)$$

Theoretically the only raw materials necessary for the entire process are coke, nitrogen, and steam. The products from reaction being NH_3, H_2, and CO, the two latter gases are by-products that in practice should be available in the form of combustible gases which would aid in keeping up either the temperature of the steaming or the temperature of the cyanizing reactions.

Results

Although the writer's own research work as well as that being carried on at the Geophysical Laboratory had shown that high pressures aid in the steaming process, it was decided to attempt the development of a process which would operate at atmospheric pressure in order to avoid the various mechanical difficulties attendant upon working at high pressures; also, at this time, the writer was limited in large scale work to a steam pressure of but 15 lbs. per sq. in.

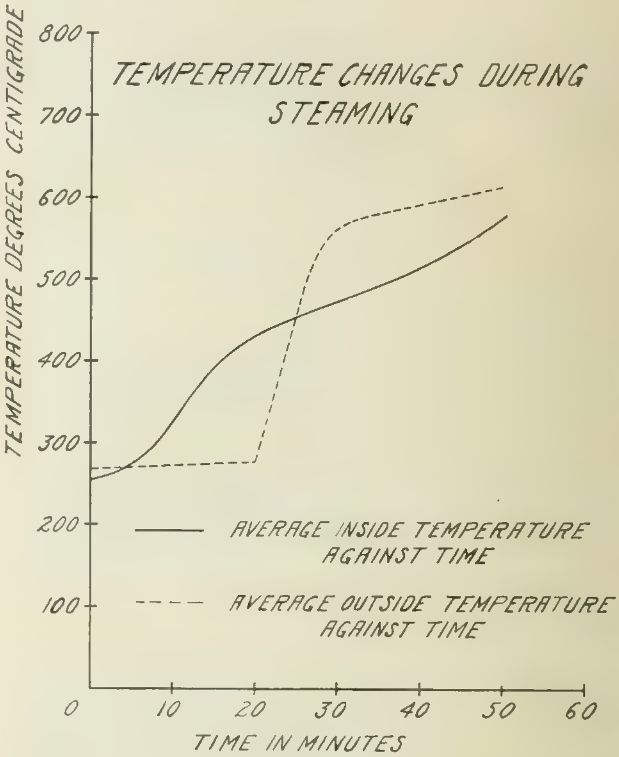

Fig. 1

Practically all work herein described was carried out either at atmospheric pressure or at the pressure of approximately one atmosphere. With batch retorts very nearly theoretical yields of ammonia from sodium cyanide were obtained. With the continuous retorts certain difficulties were at first encountered, both mechanical and chemical, due principally to ferrocyanide formation. These difficulties had been largely overcome at the time of the conclusion of the investigation (November 1918).

In the following discussion some of the results obtained with small retorts (4 in. and 8 in.) will be given, inasmuch as these results are typical and tend to throw light on the progress of the reactions during the process of steaming.

Extent to Which Temperatures of the Steaming Reaction Are Self-Sustaining

Series of experiments were undertaken in order to determine to what extent ammonia recovery could be carried on without the extension of heat. Briquets of 18 to 20 per cent cyanide content were used.

In these experiments 35 lbs. of briquets were placed in an 8-in. retort, the whole system was heated to a given temperature, the external temperature was then held constant, steam was turned on, and the temperature of the reactive mass noted.

In Table II the results from one series of runs are given. These show the maximum internal temperature attained in each case, as also the per cent recovery of ammonia.

TABLE II

RUN NO.	External Temperature (*i. e.*, Furnace Temperature) ° C.	Maximum Temperature inside Retort Due to Heat of Reaction ° C.	Per cent NH_3 Recovery
1	200	475	36
2	250	610	52
3	275	640	76
4	375	695	73
5	400	700	57

As steam was admitted to the retort the temperature rose. The rate of temperature increase depended upon the rate of steam admission and upon the rate of thermal conduction from the retort. As the steam was passed into the retort the maximum temperature was reached, after which the temperature again fell fairly rapidly and became so low that the reaction became sluggish, and ammonia evolution practically ceased. The maximum yield of ammonia was obtained with a temperature of about 650° C.; at temperatures higher than this considerable ammonia was lost through decomposition.

The rate of steam admission at the various stages of the reaction was important. Our results indicated that while a fairly large amount of steam was desirable in the early stage of the reaction, a large excess should be avoided. Best recoveries were obtained when but a slight excess of steam (not over 50 per cent) in every stage of the reaction was used.

The most satisfactory procedure was to bring the briquet mass to a temperature of from 260° to 275°, admit steam not too rapidly, then, after the temperature of the system had risen to about 450° C., to apply external heat, causing the rate of temperature increase to remain practically constant until the end of the reaction had been reached.

PROGRESS OF REACTIONS

Experiments carried out with 4-in. batch retorts had shown that practically complete ammonia recovery could be obtained in from 50 to 60 min. A series of runs was made with a retort of this type to follow the progress of the various reactions which occur in the steaming of cyanized briquets. Ten pounds of briquets were placed in each retort for each run. The temperature was raised to 260° and steam was then admitted. Each run was started under the same conditions and kept as nearly as possible under the same conditions throughout its extent. The periods of steaming were carried on progressively. The first run was carried on for 10 min., after which it was stopped and an analysis of the materials present made. The next run lasted for 20 min., the next run 30 min., the next 40 min., and the last 50 min. The data obtained in these runs are shown in Figs. 1 to 4, inclusive.

TEMPERATURE *vs.* TIME

The average temperature values for the various time intervals of the above-described set of experiments are plotted in the curves in Fig. 1. The briquet material within the retort was first brought to a temperature equilibrium which was practically the same as the external temperature (*i. e.*, the temperature of the furnace chamber). The external temperature was held constant at 260° for a period of 20 min. During that time the temperature of the briquet material was raised by the heat of reaction. At the end of 20 min. the internal temperature had risen to nearly 440°; near the end of this period, however, the rate of temperature rise had become much less rapid. The external temperature was now stepped up. At the end of 30 min. the external temperature was about 565°, while the internal temperature had risen to but 475°. By gradually raising the external temperature throughout the remainder of the run, the internal temperature was likewise caused to rise gradually.

The rate of temperature increase shown in these curves represents what has been proved by repeated experience to be a desirable rate to observe when steaming briquets in a 4-in. retort. Had stepping up the external temperature been delayed, the internal temperature would have reached a maximum (due to the heat of reaction), and a lag in the curve, or even a drop in it would have resulted. The slope of the time-temperature curve depends for most part upon two factors: first, rate of steam admission; second, cyanide content of briquets. Briquets with high cyanide content gave a rapid temperature rise in the early stages of the reaction.

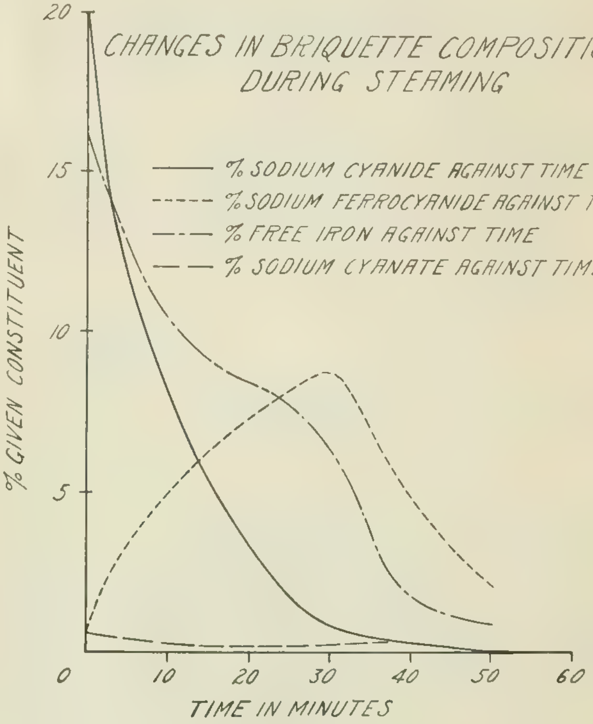

FIG. 2

PER CENT OF CONSTITUENT *vs.* TIME

In Fig. 2, the per cent of constituent is plotted as ordinate while the time in minutes is plotted as abscissa.

The original analysis of the briquets was as follows:

	Per cent		Per cent
NaCN	20.07	Na_2CO_3	36.4
NaCNO	0.48	Free iron	16.4
$Na_4FeC_6N_6$	0.00	Carbon	21.7

SODIUM CYANIDE—At the beginning of steaming the briquets contained 20.07 per cent NaCN, at the end of the first 10 min. but 7.98 per cent, and at the end of 30 min. but 0.63 per cent. The ammonia recovery at the end of this period was but 41.4 per cent of theoretical. That the fixed nitrogen, must be in some form other than NaCN or NH_3 is shown by the fact that, although but 3 per cent of the original sodium cyanide remained in briquets, 58.6 per cent of the theoretical ammonia had not been accounted for. This shows also that one is not justified in calculating ammonia liberated in hydrolysis of sodium cyanide in briquets by taking as a basis of calculation the amount of sodium cyanide remaining undecomposed in the briquets.

SODIUM CYANATE—The sodium cyanate content of the original briquets was 0.48 per cent. With beginning of steaming this value dropped to approximately 0.2 per cent where it remained until late in the period of steaming. The fact that the amount of cyanate remained so constant makes it appear that we may have an equilibrium condition and that a considerable amount of fixed nitrogen may pass through this stage. During the later periods of steaming the temporary formation of NaCNO must be fairly active, as a result of a reaction between the $Na_4FeC_6N_6$ and Na_2CO_3. This is shown by the active liberation of CO_2 gas. (Equation 22.)

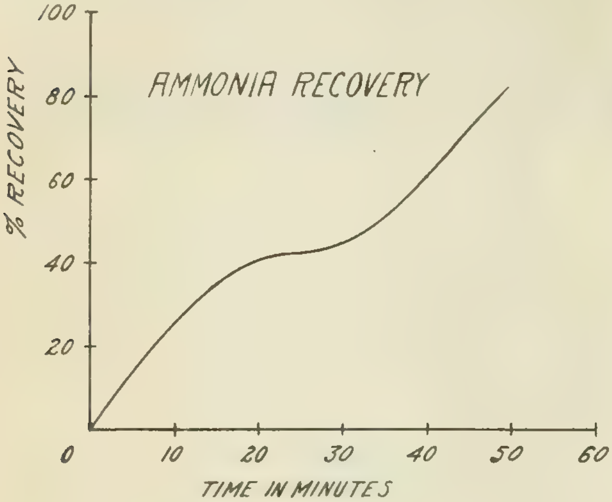

Fig. 3

SODIUM FERROCYANIDE—It was appreciated early in the research that, during an intermediate stage in the steaming reaction, not all the fixed nitrogen could be accounted for. In the early stages, as also in the later stages, practically all the fixed nitrogen could be accounted for. This fact justified the belief that nitrogen-bearing compounds must be formed during the steaming process. An investigation brought out the fact that sodium ferrocyanide is formed and that the greater percentage of the nitrogen, though not all,[8] can thus be accounted for.

Formation of ferrocyanide begins at the beginning of steaming. It increases rapidly in amount and reaches a maximum at a temperature of about 475°; above this temperature it is decomposed. Complete decomposition does not result during the 60-min. steaming period unless a temperature of about 600° C. is reached and maintained throughout the last 30 min. The rate of decomposition is dependent also upon the amount of sodium carbonate present. For a given temperature the rate of decomposition is materially increased with increase in sodium carbonate content. Considerable time is always required to drive off the last traces of ammonia. In the curve in Fig. 2, at the end of 50 min. about 2 per cent ferrocyanide remained in the briquets, while the recovery of ammonia (Fig. 3) at this point had reached 84.8 per cent.

IRON—At the beginning of steaming the briquets contained 16.4 per cent free iron. Oxidation began at once and continued throughout the run. At the end of 20 min. (temperature about 433° C.) over half the iron had been oxidized. As the temperature was raised the rate of oxidation increased; Fe_3O_4 was now formed. At the end of 50 min., but 0.77 per cent free iron remained.

At the conclusion of a steaming run practically all the iron present in the briquets was in the form of oxide. This fact does not hinder the recyanization of the steamed briquets, for it has been found that, even though pure, finely divided iron is used in the making of briquets, this iron becomes almost completely oxidized during the process of kneading and drying. During the process of cyanization this oxide is reduced (in some instances only partly) and serves its function as a catalyst in the reaction. The oxidation of iron during steaming offers no disadvantages except that carbon must later be used up in order to reduce the oxide when the briquets are subjected to the process of recyanizing. As far as the total effect on steaming is concerned, the oxidation of iron is advantageous in that the reaction is highly exothermic:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2 + 200{,}800 \text{ cal.} \qquad (18)$$

and is the source of much of the internal heat which is generated during steaming.

Ammonia Recovery *vs.* Time

The rate of ammonia evolution (Fig. 3) was high during the first 20 min. of the reaction; at the end of this period the temperature had reached 433°, 83 per cent of the cyanide had disappeared, and had formed 6.67 per cent ferrocyanide, while the ammonia recovery was but 39.5 per cent of the theoretical. During the next 10-min. interval, in which the temperature had increased to 473°, the ammonia evolution was low; but 1.9 per cent of the total ammonia was given off. During this interval the cyanide content had dropped to very nearly a minimum, while the ferrocyanide content had risen to a maximum.

Above this temperature the rate of evolution again increased very nearly to its original value. It is noted that this increase in evolution of gas begins with the decomposition of ferrocyanide and, further, that the high evolution of gas is a direct result of the decomposition of the sodium ferrocyanide.

Composition of Gases Evolved during Steaming

Curves showing the rate of gas evolution during steaming operations are given in Fig. 4.

At the end of the 10-min. period the gas composition was 95 per cent H_2, 0.7 per cent N_2, 4.3 per cent CO. This gas composition indicated that for most part the following reactions were in progress:

$$2NaCN + 4H_2O = 2NH_3 + Na_2CO_3 + H_2 + CO \qquad (19)$$
$$\text{and } C + H_2O = CO + H_2 \qquad (20)$$

At the end of the 30-min. period the gas composition was 1.3 per cent N_2, 5.4 per cent CO, 93.3 per cent H_2; Reaction 19 was decreasing in extent and Reaction 21

$$Na_4FeC_6N_6 = 4NaCN + Fe + 2C + N_2 \qquad (21)$$

was beginning. At the end of the 50-min. period the gas composition was: N_2 1 per cent, CO 2.7 per cent, CO_2 8.1 per cent, H_2 88.2 per cent.

This analysis shows that very little $Na_4FeC_6N_6$ was decomposing according to Equation 21, but instead was reacting according to Equation 22:

$$Na_4FeC_6N_6 + Na_2CO_3 = 5NaCN + NaCNO + Fe + CO_2 \qquad (22)$$

These results indicate why it is possible to obtain high yields of ammonia even though the sodium cyanide of briquets may be converted to sodium ferrocyanide.

Comparison of Value on Curves

The time factors of all the curves have been plotted as abscissas, and all on the same scale. It is possible therefore to compare directly all corresponding points on these different curves.

Large Scale Work

Repeated experimental runs made with an 8-in. batch retort had shown that from 85 to 100 per cent ammonia recovery could be attained. It further appeared that from 95 to 100 per cent recovery could be obtained, provided sufficient care were taken and sufficient time allowed for the removal of the last traces of ammonia.

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[8] The writer has not as yet been able to determine in what forms all nitrogen exists during this period.

The results obtained in a series of runs with an 8-in. batch retort of about 190 lbs. briquet capacity are given in Table III.

TABLE III

NaCN in Briquets Per cent	Time of Steaming, Min.	Temperature Range, ° C.	Per cent Ammonia Recovered Based on Total N Content of Briquets	Per cent Recovery Based on NaCN in Briquets
17.09	150	260–675	82.9	84.5
19.25	110	260–675	87.6	93.1
18.19	115	250–590	86.6	88.9
17.80	60	130–680	88.5	91.5
19.84	75	115–605	94.6	96.3
23.76	210	245–710	90.1	93.5
25.79	175	260–685	100.0	102.5
25.91	158	260–710	89.6	91.6
25.75	155	260–685	88.1	91.1
20.79	210	260–690	83.0	86.3
19.99	155	250–675	94.1	96.3
			AVERAGE	91.2

These runs are not typical of runs made primarily for high recovery. They were strictly experimental and were made to determine the effect of varying different factors connected with the reactions, such as the effect of different percentages of cyanide in briquets, different amounts of steam during different stages of the reaction, etc.; also for determining the extent to which the reactions were self-sustaining thermally. In these runs absolutely dry briquets were not used in all cases, which would tend to lower the ammonia recovery. The average ammonia recovery based upon NaCN content of the briquet in the nine runs cited was 91.2 per cent. It was found that with the 8-in. retort of this type, giving 90 to 100 per cent recovery, approximately 3 hrs. would be required to complete the steaming process. Allowing 1 hr. for charging and discharging, the daily capacity of the steaming retort would be about 1140 lbs., which was approximately the daily capacity of a single cyanizing retort of the Saltville type.

A 10-in. retort 10 ft. in length was next tried out. Two runs were made with this retort. In one run 99 per cent and in the other 100 per cent recovery was obtained. The total time of steaming was 5 hrs. This retort had a capacity of 5.45 cu. ft. and would hold approximately 300 lbs. of briquets. Allowing 6 hrs. for each steaming operation, the daily capacity of this retort was 1200 lbs. of briquets. This was ample to care for the output from one cyanizing retort.

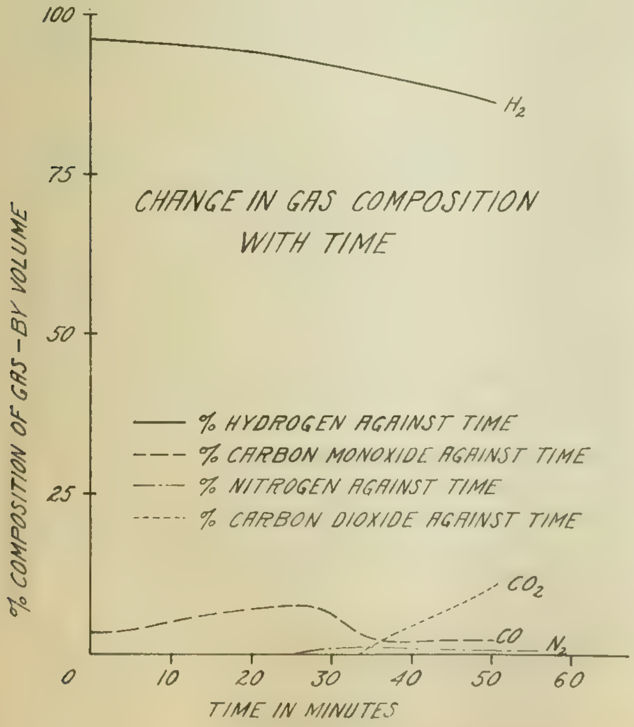

FIG. 4

Large steaming retorts looked so promising that two 16-in. retorts were next constructed and put into use. The capacity of each of these retorts was approximately 11.6 cu. ft.; they could hold approximately 640 lbs. of briquets. A steaming cycle could be made with a 16-in. retort in about 6 hrs., giving it a daily capacity of 1920 lbs., nearly enough to take care of the output from two cyanizing retorts.

The first eight runs with the 16-in. retorts gave low recoveries which ranged from 40 to 68 per cent. The low yields were due for most part to inexperience in operating the 16-in. steamer, which behaved decidedly differently from the 8- and 10-in. steamers, the main difference being due to the low thermal conductivity of the briquets which required a much longer time for heat transfer throughout the mass.

The next four consecutive runs with the 16-in. steamer gave results as follows:

Temperature Limits ° C.	Per cent Recovery Based on NaCN Content of Briquets
285–440	83.9
250–550	70.2
320–700	93.7
200–587	84.5

At this point work with batch retorts was temporarily held up while attention was given to the operation of steamers of the continuous type.

CONTINUOUS STEAMERS

Throughout the entire period of this investigation experiments were carried on with continuous steamers.

Vertical steamers 8 in. in diameter were used. Certain difficulties developed, due mainly to sticking of briquets caused by ferrocyanide hydrate formation in the upper part of the retort. These difficulties had not been entirely overcome at the close of the investigation.

An 8-in. horizontal steamer, 10 ft. in length, of the continuous type, was developed by Lieutenant Lowe. Briquets were mechanically carried through the retort by means of a screw conveyor. This steamer was put into operation just before the close of this work and but a single continuous run was made. Briquets were conveyed directly, while hot, from a cyanizing retort into this steamer. The internal temperatures ranged from about 300° C. at the feed to about 525° C. at the discharge end of the retort. The temperature external to the retort was 650° C. No mechanical difficulties whatever were experienced during this run of 20 hrs. The rate of feed was approximately 40 lbs. of briquets per hr., which was the rate of discharge from the one cyanizer in use at that time.

Based upon the ammonia equivalent of NaCN and NaCNO in the briquets used, the ammonia recovery was 97.8 per cent. The signing of the Armistice terminated the work at this point.

Fellowships in Mining Research

The Coöperative Department of Mining Engineering of Carnegie Institute of Technology, Pittsburgh, Pa., has announced the offer of two fellowships in mining research and two in teaching and research, in coöperation with the Pittsburgh Experiment Station of the U. S. Bureau of Mines. The value of each fellowship is $750 per year of ten months, beginning July 1, for the position of research fellow and August 1 for teaching fellow. Investigations will be on the following subjects: acid mine waters, shooting coal, spontaneous combustion and coal storage, geology, by-products coking, utilization of coal, and coal mining. All the time of the research fellow is to be devoted to work in the Experimental Station of the Bureau of Mines, while the position of teaching fellow includes ten hours a week of teaching work in mining and the balance of work in the Experimental Station.

Relative Sweetness of Invert Sugar[1,2]

By J. W. Sale and W. W. Skinner[3]

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Although it is commonly believed that sugar may be conserved by inverting it, experiments described in this paper show that if sucrose is assigned a sweetening value of 100, the sweetening value of invert sugar is only 85. Since 100 units of sucrose by inversion become 105 units of invert sugar, the net loss in sweetening power by the inversion of 100 units of sucrose is about 11 units. For some purposes, such as in the manufacture of candy and certain bottlers' sirups, or concentrates from which bottlers' sirups are prepared, it may be advantageous to use a sirup which has been partly inverted because it does not crystallize so easily as an ordinary sugar sirup, thus permitting the use of a denser and therefore a better keeping sirup.

Invert sugar sirup in which the sucrose, or ordinary sugar, has been almost completely inverted can be prepared so that it is practically devoid of flavor, provided less acid is employed than is ordinarily recommended and the time of heating is reduced to a minimum. The amount of acid recommended in the preparation of a practically flavorless and colorless invert sirup is 0.013 per cent of weight of C. P. hydrochloric acid (37 per cent) based on the weight of sugar and water taken. Boiling for 20 min. with this amount of acid will be sufficient to invert practically all of the sucrose. 0.021 per cent by weight of tartaric acid crystals (99.5 per cent) caused an inversion of 96 per cent when the solution was boiled 40 min. At the end of 20 min., only 67 per cent of the sucrose (ordinary sugar) was inverted. These data were obtained on sugar solutions made by boiling equal weights of sugar and water. The sirup obtained in this way will be reduced in volume and have a density of about 30° Bé. When less water is used to dissolve the sugar, the temperature at which the solution boils will be higher and the color and flavor will be increased.

Invert sugar sirups inverted with hydrochloric and tartaric acids, respectively, were practically without color or flavor, but gave a slightly unpleasant harsh sensation, which, however, was not produced by the finished beverage.

Invert sirup prepared with invertase and concentrated by boiling under reduced pressure was practically colorless, possessed only a slight candy flavor, and was remarkably smooth when taken in the mouth. This sirup was therefore superior to the invert sirups prepared with acid. Since invertase is now obtainable in commercial quantities, this method of preparing invert sirup is recommended. Invert sirup having a density of 42° Bé., prepared with invertase, will contain approximately 0.001 per cent of added protein nitrogen.

Invert sirups which are practically without flavor or color make satisfactory bottled sodas. However, invert sirups prepared according to the usual formulas and possessing a decided candy flavor do not make strictly first-class lemon sodas, orange sodas, or other delicately flavored products.

INFORMATION to the effect that sugar may be conserved by the process of inversion has been widely disseminated in trade and other publications during the past two or three years. As a result, the Bureau of Chemistry has received many inquiries for specific information on the subject. It is commonly stated that a net increase in sweetening power of 30 per cent is gained by the conversion of sucrose into invert sugar. For this reason the use of invert sugar sirup in the manufacture of bottled sodas, ice cream, etc., has been advocated, and there is no doubt that large quantities of it have been used by bottlers in the belief that sugar was thus being conserved. The question of the sweetness of invert sugar as compared with that of sucrose or ordinary sugar, therefore, is a matter of some commercial importance and of much scientific interest.

As it seemed that a difference of 30 per cent in the sweetening power of two sugar solutions should be detected with certainty by anyone with a normal sense of taste, some experiments were undertaken to test the validity of the claims for the sweetness of invert sugar. The chemist who is accustomed to proceed along exact analytical lines usually accepts with reluctance conclusions based on a series of tests which depend upon the sense of taste, unsupported by other confirmatory data. Nevertheless, successful experiments along this line have been recorded by chemists, and more particularly by psychologists who have developed standard psychophysical procedures for the determination of stimulus limen, difference limen, etc. For example, Richards,[4] who worked with supraliminal solutions, determined when a given quantity of acid was neutralized by alkali so successfully that the average amount of acid found in six tests was 99.9 per cent of the amount actually present. The greatest variation from the average was 1 per cent. He stated that in this method of analysis a degree of accuracy exceeding some which are seriously applied as quantitatively useful was reached. Richards' work on acids, as well as that of Corin,[5] of Kahlenberg,[6] of Kastle,[7] and of Crozier,[8] was made the object of further study by Gibson and Hartman,[9] who applied the stimulus limen as a criterion of the sapidity of certain acids, and used a standard psychophysical procedure. While the sense of taste and the sense of smell receive little consideration in the average analytical chemical laboratory, they are employed by manufacturers of foods, flavors, and perfumes in obtaining fairly accurate comparative data. The taste and aroma of vanilla and of lemon extracts, of bottled ginger ale, of coffee, of tea, and of many other products, largely determine the quality and the price at which they are sold, irrespective of any quantitative chemical data which may be obtained.

In some previous experiments[10] made in the Water and Beverage Laboratory, the stimulus limens of four chemically pure sugars were obtained and the relative sweetness calculated, with the following results: sucrose = 100; dextrose = 50; levulose = 150; maltose = 60. Paul[11] compared the sweetness of several sugars with that of sucrose. His data, recalculated to a basis of sucrose = 100, are as follows: dextrose = 52; levulose = 103; lactose = 28.

The Inversion of Sucrose

When 342.236 (= molecular weight) units of sucrose or ordinary sugar are inverted, 180.126 units of dextrose and

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[1] Received February 9, 1922.

[2] Published by permission of the Secretary of Agriculture.

[3] Assistant Chief, Bureau of Chemistry.

[4] *Am. Chem. J.*, **20** (1898), 121.

[5] *Arch. biol.*, **8** (1888), 121.

[6] Univ. Wisconsin, *Bull.* **2** (1898), 2; *J. Phys. Chem.*, **4** (1900), 33.

[7] *Am. Chem. J.*, **20** (1898), 466.

[8] *J. Comp. Neurol.*, **26** (1916), 453.

[9] *Am. J. Psychol.*, **30** (1919), 311.

[10] *Southern Carbonator and Bottler*, June **1918**.

[11] *Chem.-Ztg.*, **45** (1921), 705.

180.126 units of levulose are obtained theoretically. The mixture of dextrose and levulose is known as invert sugar. Since 342.236 units of ordinary sugar produce 360.252 (molecular weight) units of invert sugar, there is a gain in actual weight of sugar of a little over 5 per cent

$$\left(\frac{360.252}{342.236} = 1.0526\right).$$

If sucrose = 100, dextrose = 50, and levulose = 150, then by calculation, invert sugar = 100, that is, a unit weight of sucrose and a unit weight of invert sugar are equally sweet. Since there is an actual gain in weight of sugar in the process of inversion of 5 per cent, it follows that there might be a small gain in sweetness. If Paul's figures, *viz.*, sucrose = 100, dextrose = 52, levulose = 103, are accepted, then by calculation invert sugar = 78. The writers have been unable to confirm Paul's value for levulose. However, a conclusion as to the relative sweetness of invert sugar and sucrose should be based on direct experimental evidence, rather than calculated from the relative sweetness of dextrose and levulose, since the character of a sucrose solution changes during the process of inversion. As will be shown, this change depends to some extent upon the method of inversion employed. The most apparent change is in the flavor and there is also a possibility of a partial destruction of levulose.

PREPARATION OF SIRUPS

Five samples of ordinary highly refined cane sugar, weighing 1 kg. each, were made up into sirups according to the methods described below. All weights of sugar and sirup were corrected for displacement of air. The sugar used was analyzed by the method of double polarization at 20° C. and was found to be 99.99 per cent pure. After being adjusted to the desired concentrations, the sirups were analyzed with a saccharimeter and the results obtained were checked by the copper method described in "A. O. A. C. Methods of Analysis."

Sample 1 was dissolved in 1 l. of distilled water; 5.5 cc. of 0.5 *N* hydrochloric acid (0.013 per cent by weight of C. P. hydrochloric acid (37 per cent), based on weight of sugar and water taken) were added; and the sirup was boiled in a glass flask for 20 min. After cooling to room temperature (29° C.) the sirup was diluted with distilled water to such a volume that 1 cc. contained theoretically 0.5 g. of invert sugar. This sirup was designated as Sirup 1.

Sample 2 was dissolved in 1 l. of water; 5.5 cc. of *N* tartaric acid (0.021 per cent by weight of C. P. tartaric acid crystals (99.5 per cent)) were added; and the solution was boiled in a glass flask for 40 min. Previous experience had shown that in a 20-min. period of boiling, with this amount of tartaric acid, only about 67 per cent of the sucrose was inverted, but in a 40-min. period of boiling the inversion is over 95 per cent complete. The sirup which had been boiled 40 min. was adjusted to the same theoretical strength as Sirup 1 and was designated as Sirup 2.

Sample 3 was dissolved in 1 l. of water, and adjusted at room temperature to such a volume that 1 cc. contained theoretically 0.5 g. of sucrose (ordinary sugar). This sirup which was an ordinary sugar sirup (not inverted) was designated as Sirup 3.

Samples 4 and 5[12] were combined and dissolved in 6 l. of distilled water, 100 cc. of autolyzed yeast extract were added, and the sugar solution was allowed to stand at room temperature for 48 hrs. At the end of this time the inverted sugar solution was heated to 90° C., mixed with about 25 g. of Norit, filtered, and the carbon washed free of sugar. The filtrate was divided in two equal portions. One portion was concentrated by boiling at atmospheric pressure and after cooling was adjusted to such a volume that 1 cc. contained theoretically 0.5 g. of invert sugar. This sirup was designated as Sirup 4. The other portion was concentrated by boiling in a partial vacuum (pressure of 1 to 2 in.) and finally adjusted to such a volume that 1 cc. contained theoretically 0.5 g. of invert sugar. The sirup was designated as Sirup 5.

COMPOSITION OF SIRUPS

After being adjusted to such volumes that 1 cc. at 29° C. contained by calculation 0.5 g. of sugar, the sirups were analyzed with a saccharimeter and the results checked by the copper method. The results obtained are recorded in Table I.

TABLE I—COMPOSITION OF SIRUPS USED FOR COMPARING SWEETNESS

(Percentage of sugar based on weights of sugar and specific gravity of sirups = 42.2)

	By Saccharimeter			By Copper		
Sirup No.	Sucrose[1] Per cent	Invert Sugar Per cent	Total Sugar Per cent	Sucrose[1] Per cent	Invert Sugar Per cent	Total Sugar Per cent
1	0.9	42.6	43.5	0.5	40.9	41.4
2	1.6	40.5	42.2	2.3	39.5	41.9
3	42.1	0.0	42.1	41.1	0.5	41.6
4	0.8	41.6	42.4	0.1	41.4	41.5
5	0.1	42.9	43.0	0.0	41.3	41.3

[1] Ordinary sugar.

In calculating the percentage of invert sugar from the readings on the saccharimeter, which were made at 29° C., the value for the specific rotation of levulose found by Vosburgh[13] for a concentration of 5.0 g. per 100 cc. at 29° C. was used. It is of interest to note that the results obtained by the saccharimeter are consistently higher than those obtained by the copper method. Sirups 1, 4, and 5 were satisfactorily inverted. Sirup 2 was inverted only to the extent of 96 per cent, based on the total sugar found by the saccharimeter. This lack of complete inversion, however, did not introduce any serious error in the tasting experiments.

TASTING EXPERIMENTS

The taste sensation is influenced by many factors[14] among which are (1) strength of solutions employed, (2) amount of solutions applied, (3) extent of surface excited, (4) duration of the application, (5) temperature of the solutions, (6) state of rest or movement of the tongue, (7) nature of preceding stimuli, (8) adaptation, (9) fatigue, (10) touch, (11) smell, (12) sight. While these and other factors have been kept in mind, a strict psychophysical procedure, by controlling the touch, temperature, and movement factors, and by applying minute amounts of the various solutions to single papilla by eliminating smell by closing the nostrils, etc., and thus determining stimulus limen, was not followed. Instead Richards' procedure, using supraliminal solutions of a concentration previously determined to be of special significance, was chosen for comparison. Richards' conclusions as to the sapidity of certain acids were confirmed by Gibson and Hartman[9] who used the standard but more laborious technic of the psychologist. Moreover, in expressing and interpreting results in the subsequent portion of this paper, the use of technical or psychophysical terms has been avoided with a view to making the experiments more intelligible to the food manufacturer, especially the bottler.

The five sirups, therefore, were prepared and adjusted to such volumes that each cubic centimeter contained theoretically 0.5 g. of sugar. The analysis of these sirups by two methods showed that they were, in fact, of the theoretical strength within reasonable limits. The final volumes of the sirups were in the ratio of 100 volumes for the sucrose sirup and 105 volumes for the invert sirups, equal amounts of sucrose having been used in their preparation. The sourness of Sirups 3, 4, and 5 was made equal to that of Sirups 1 and 2 by the addition of an equivalent amount of acid.

Solutions of the sirups varying from 2 to 3 per cent in strength were made with distilled water. These strengths proved on preliminary testing to be most satisfactory for the final comparisons, since the difference in limen of solutions of these concentrations was found consistently to be 5 per cent, whereas higher or lower concentrations were less satisfactory. Portions of the diluted solutions were emptied into beakers and the beakers shuffled. A spoon with a capacity of 3.5 cc. was used to convey the solutions to the mouth. Sipping from the beaker, drawing a measured quantity of solution into the mouth from a bent glass tube, and other methods were tried, but were discarded in favor of the spoon. Before each sweet solution was tasted, the mouth was rinsed out with a spoonful of distilled water. After tasting, the solutions were arranged in the order of their relative sweetness. Due regard was paid to the factor of fatigue and to the nature of preceding stimuli by the duration of the tests and by allowing several hours to elapse after a meal before beginning the tests. While not all the factors enumerated were reduced to a minimum, they were kept very constant. The individual sensitiveness to taste sensation probably does not vary greatly with the individual. Yet as the tests proceeded a variation in ability to make nice discriminations in taste sensation was noticed. This variation was probably due to quality of perception rather than to quality of taste sense, since a noticeable improvement was made by the observers in their ability to make correct decisions when several sucrose solutions of slightly different strengths were compared.

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[12] Mr. C. F. Walton, of the Carbohydrate Laboratory, prepared Sirups 4 and 5, and also confirmed certain of the analytical data reported.

[13] "Specific Rotation of Levulose," *J. Am. Chem. Soc.*, **42** (1920), 1696.

[14] Hollingworth and Poffenberger, "The Sense of Taste," 44.

The results obtained are recorded in Table II.

TABLE II—RESULTS OF TASTING EXPERIMENTS

Kind of Solution[1]	Sugar in 100 Cc. of Solution[2] Grams	Relative Strength of Solutions	Order of Relative Sweetness by Tasting[3]				
			Observers 1	2	3	4	Predominating Opinion
		TRIAL A					
Sucrose 3	2.0	100	*a*	*a*	*a*	*a*	*a*
Sucrose 3	2.2	110	*b*	*b*	*c*	*b*	*b*
Sucrose 3	2.5	125	*c*	*c*	*b*	*c*	*c*
		TRIAL B					
Sucrose 3	2.0	100	*a*	*a*	*a*	*a*	*a*
Sucrose 3	2.1	105	*b*	*b*	*b*	*b*	*b*
Sucrose 3	2.3	115	*c*	*c*	*c*	*c*	*c*
		TRIAL C					
Invert 1	2.0	100	*a*	*a*	*a*	*a*	*a*
Invert 2	2.5	125	*b*	*b*	*b*	*b*	*b*
		TRIAL D					
Invert 1	2.0	100	*b*	*a*	*a*		*a*
Invert 2	2.2	110	*a*	*b*	*b*		*b*
		TRIAL E					
Invert 1	2.0	100	*a*	*a*	*a*	*a*	*a*
Invert 2	2.0	100	*a*	*a*	*a*	*a*	*a*
Sucrose 3	2.0	100	*b*	*b*	*b*	*b*	*b*
Invert 4	2.0	100	*a*	*a*	*a*	*a*	*a*
Invert 5	2.0	100	*a*	*a*	*a*	*a*	*a*
		TRIAL F					
Invert 1	2.0	100	*a*	*a*	*a*	*a*	*a*
Invert 2	2.0	100	*a*	*a*	*a*	*a*	*a*
Sucrose 3	2.0	100	*b*	*b*	*b*	*b*	*b*
		TRIAL G					
Invert 1	2.1	105	*a*	*a*	*a*	*a*	*a*
Invert 2	2.1	105	*a*	*a*	*a*	*a*	*a*
Sucrose 3	2.0	100	*b*	*b*	*b*	*a*	*b*
		TRIAL H					
Invert 2	2.2	110	*b*	*a*	*a*	*a*	*a*
Sucrose 3	2.0	100	*b*	*b*	*b*	*b*	*b*
Invert 4	2.2	110	*a*	*b*	*a*	*b*	*a*, *b*
		TRIAL I					
Invert 1	3.0	150	*c*	*c*	*c*		*c*
Invert 2	2.5	125	*b*	*b*	*a*		*b*
Sucrose 3	2.0	100	*a*	*a*	*b*		*a*

[1] Invert 1, hydrochloric acid used for inversion.
Invert 2, tartaric acid used for inversion.
Sucrose 3, plain sucrose solution.
Invert 4, invertase used for inversion, concentrated at atmospheric pressure.
Invert 5, invertase used for inversion, concentrated in vacuum.

[2] Error is negligible if figures in this column are termed per cent by weight of sugar.

[3] *a* = least sweet; *b* = sweeter than *a*; *c* = sweeter than *b*

INTERPRETATION OF RESULTS

When two solutions of different sugars but of the same percentage strengths are tasted and designated *a* and *b* according to their relative sweetness, *a* being less sweet than *b*, quantitative data can be obtained by diluting the sweeter solution until no difference can be detected in the sweetness of the two solutions. The probable error can be obtained from the different percentages of a given sugar in two solutions classed as being equally sweet.

Trials A and B in Table II show that it is possible to distinguish, by tasting, a 2 per cent sucrose solution from a 2.1 per cent solution, the relative strengths of the two solutions being 100 and 105, respectively. This and larger differences can be detected consistently. Trials C and D show that a 2 per cent invert sugar solution can be distinguished from a 2.2 per cent invert sugar solution, and that larger differences can be distinguished consistently. Invert sugar prepared in different ways was used for these comparisons, but later tests showed that the methods of preparing the two sirups did not affect their sweetness. Trials E and F show conclusively that the four invert sugar solutions each containing 2 per cent of invert sugar were equally sweet, although they were prepared in different ways. Furthermore, a 2 per cent sucrose solution is shown to be sweeter than any of the 2 per cent invert sugar solutions. Inspection of the data in Trials G, H, and I indicates how much sweeter sucrose is than invert sugar at a concentration of about 2 per cent. Trial G shows that a 2 per cent sucrose solution is sweeter than a 2.1 per cent invert sugar solution, Trial H that it is even sweeter than a 2.2 per cent invert sugar solution, and Trial I that it is less sweet than a 2.5 per cent invert sugar solution. Evidently, then, a 2 per cent sucrose solution is about as sweet as a 2.35 per cent invert sugar solution prepared according to one of the methods which were used. If sucrose is assigned a value of 100, invert sugar equals 85, or, expressed in another way, 117 units of invert sugar would have the same sweetening power as 100 units of sucrose.

INFLUENCE OF FLAVOR

Sirups 1 and 2 were prepared in such a way that they were practically devoid of the flavor which is ordinarily regarded as a characteristic of invert sirups. They gave, however, a slightly harsh or rough sensation, which is undesirable. This harsh sensation was not eliminated by neutralizing the residual acidity of the sirup with alkali. Sirup 4, prepared with invertase and reduced in volume by boiling at atmospheric pressure, possessed a very marked flavor suggesting candy. Sirup 5, prepared with invertase and reduced in volume by boiling in a partial vacuum, possessed a slight though distinct candy flavor. Sirups 4 and 5 did not produce the slightly harsh sensation which was given by the sirups inverted with acid. In fact, they were remarkably smooth, agreeable, and honey-like. Of the four invert sirups, Sample 5 was the most pleasing to the senses.

The appearance, flavor, and taste of the finished sirups are summarized in Table III.

TABLE III—APPEARANCE, FLAVOR, AND TASTE OF FINISHED SIRUPS

SIRUP No.	METHOD OF PREPARATION	APPEARANCE	FLAVOR	TASTE AND TOUCH
1	Inverted with hydrochloric acid	Colorless	Practically none	Slightly harsh, sweet
2	Inverted with tartaric acid	Slight yellow tinge	Practically none	Slightly harsh, sweet
3	Not inverted	Colorless	None	Neutral, sweet
4	Inverted with invertase concentrated by boiling at atmospheric pressure	Deep yellow	Marked candy flavor	Smooth, sweet
5	Inverted with invertase concentrated by boiling under reduced pressure	Slight yellow tinge	Slight candy flavor	Smooth, sweet

QUALITY OF BOTTLED SODAS MADE WITH INVERT SIRUP

Bottled sodas were prepared with all five sirups. Root beer, ginger ale, and lemon flavors were selected as typical of the various types and also because both ginger and lemon are especially well adapted to such comparisons, having such delicate flavors, or aromas, that the slightest off-flavor in any of the ingredients becomes quickly noticeable in the finished beverage. All the sirups except Sirup 4 made equally satisfactory beverages. The slightly harsh sensation which had been given by Sirups 1 and 2 (inverted with acid) was not produced by the finished beverage. Lemon and ginger ale sodas made with Sirup 4 had a distinct off-flavor which rendered them inferior in quality to the other bottled sodas. The root beer made with Sirup 4 was much less affected, though it was considered somewhat inferior to the root beer made with ordinary sugar sirup and with the other invert sirups. Bottled sodas made with invert sirup were stored at room temperature over a period of two months of very warm weather. Their keeping quality was satisfactory.

A Study of Methods of Minimizing Shrinkage in Shell Eggs during Storage[1,2]

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The present study is preliminary to a general investigation of the cause and prevention of the development of cold storage odor and taste in eggs. It deals solely with the relative efficiencies of various sealing agents for preventing the escape of substances, mainly water vapor, from within the shell.

Observations have been made of loss in weight of treated and untreated eggs kept at room or higher temperature for varying periods of time.

Treatment with heated air for 5 min. fails to reduce shrinkage during storage. Immersion for short periods in heated or unheated aqueous solutions of mineral or organic acids, mineral salts, or soap fails to check shrinkage appreciably.

Tests with drying, semidrying, and nondrying vegetable oils, nondrying animal oils, and mineral oils do not justify the conclusion that sealing properties can be definitely correlated with drying properties. Cottonseed oil apparently makes a very good sealing agent. The sealing value of mineral oi s bears a definite relation to grade, as defined by gravity, flash point, and viscosity tests. Given equal sealing value, mineral oils should prove better than vegetable oils because they are less likely to impart odor and are less subject to change during storage.

The addition of 1 or 2 per cent of soap to a mineral oil markedly increases its sealing value. Nothing is to be gained by the addition of gums, waxes, or rosin to relatively heavy mineral oils.

THE most noticeable of the changes which take place in eggs during cold storage are a loss in weight, the development of a characteristic odor and taste, a weakening of the membrane surrounding the yolk, and a change in the consistency of the white. Evaporation of water, which is an invariable accompaniment of the cold storage condition, accounts for practically all of the shrinkage observed. The second change may be due to absorption of odors and flavors from without, or to the production of odorous substances within the shell membrane, or to both. The influence of foreign substances is facilitated by the natural porosity of the shell and the affinity of the yolk for odors and flavors. Many in the trade believe that the so-called "cold storage taste" in eggs is due mainly to the absorption of odors from the egg cases, excelsior, and strawboard fillers and flats used in packing the eggs for storage. A small amount of experimental evidence[4] supports such an assumption, but adequate scientific data covering this point have not yet been presented. Enzyme action, which proceeds very slowly at the low temperature of storage, causes the weakening of the membrane surrounding the yolk and the change in the consistency of the white.

In connection with a study of methods of preserving eggs by sealing the pores of the shell, Jones and DuBois[5] made a thorough search through the literature bearing on the general subject of egg preservation and report an extensive bibliography. As a result of their experiments they conclude that aluminium soap applied in a gasoline (or preferably a pentane) solution is an ideal substance for closing the pores of the shell. The method outlined is not a simple one, however.

Several patented processes of treating eggs which have been developed within the last few years are being used commercially with apparent success. In general, the processes consist in dipping the eggs into a hot bath of an oil or oil mixture for a few seconds and then usually into a similar cool bath. After draining, the eggs are packed in cases provided with well-made fillers and placed in storage. The treatment retards shrinkage during storage and as a rule the eggs bring a higher price than unprocessed storage eggs. It is claimed that treated eggs keep well, even at ordinary temperatures. Such an enhanced keeping quality is, of course, most desirable, especially in export shipments, as many ships have inadequate refrigeration facilities.

Scope of Investigation

The present study was conducted as a preliminary to a general investigation of the causes and prevention of the development of the cold storage odor and taste in storage eggs. Rendering the shell membrane impervious to gases and vapors would provide a means for determining the extent to which the packing materials contribute to the characteristic taste. A membrane might be impermeable to water vapor, yet permit the passage of odorous volatile substances. This paper deals solely with the attempt to determine the relative efficiencies of various sealing agents for preventing the escape of substances, mainly water vapor, from within the shell. The treatments which are here found to be distinctly superior may be applied in the study of the related problem of preventing the entrance of foreign odors.

Separate lots of eggs were subjected to the action of heated air and to immersion in aqueous solutions, in oils, and in oily mixtures. Observations were made of the losses in weight of these eggs and of untreated eggs held at room and higher temperatures for periods up to 35 days.

Heat Treatments

The air treatments (Table I) showed that heating of the surface for 5 sec. failed to reduce the shrinkage during stor-

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[1] Received February 13, 1922.

[2] Published by permission of the Secretary of Agriculture.

[3] Food Research Chemist, Bureau of Chemistry.

[4] "Commercial Preservation of Eggs by Cold Storage," *U. S. Dept. Agr., Bull.* **775** (1919), 33.

[5] This Journal, **12** (1920), 751.

TABLE I—EFFECT OF HOT AIR TREATMENT OF EGGS

	After Storage for 35 Days at Room Temperature	
EGGS	Loss in Weight Per cent	Comparative Loss in Treated and Untreated Eggs (Untreated = 100)
Treated with air at 320° C. for 5 sec.	8.4	105.0
Treated with air at 610° C. for 5 sec.	7.8	97.5
Untreated	8.0	100.0

age. In the remaining experiments eggs were treated by immersion for different periods of time in fluid media, either heated or unheated. The results of the heat treatments, though scant, suggest that the value in the use of elevated temperatures in the fluid immersion tests will lie in the action of the heat in facilitating penetration of the fluid into the pores of the shell rather than in any tendency to seal the pores by a hardening of the shell membranes or coagulation of the proteins.

AQUEOUS SOLUTIONS

Immersion of eggs for short intervals in heated and unheated aqueous solutions of mineral and organic acids, mineral salts, and soap, as shown in Table II, failed to check shrinkage appreciably. The sulfuric acid treatment was by far the most effective, for, whereas the loss in the eggs treated with 5 per cent sulfuric acid solution was 26.4 per cent of that in the case of untreated eggs, the losses in those treated with the other solutions ranged from 66.4 to 106.4 per cent. Dilute solutions of sulfuric, orthophosphoric, and oxalic acids react with calcium carbonate to form difficultly soluble salts of calcium. The new salt forms a coating over the entire exposed surface of the carbonate, thus tending to stop the reaction. Apparently some such chemical action occurred in this experiment, as the acids mentioned produced a measurable effect upon the shrinkage of eggs thus treated. It is possible that the size and, to a smaller extent, the number of the pores were somewhat reduced by these precipitates. The slight beneficial effect of the aqueous solutions of the different salts employed in this test was due to mechanical plugging of the pores. The soap mixture[6] was practically without effect upon shrinkage. A similar experiment in which cottonseed oil was used as the immersion fluid demonstrated that this oil is markedly superior to the aqueous solutions. The loss in eggs treated with the oil was but 4.5 per cent of that observed in the case of the untreated eggs.

OILS

The value of an oil as a sealing agent may be expected to depend upon its viscosity, drying properties, odor, tendency to become rancid, etc. Eggs were treated with different oils representing drying, semidrying, and nondrying vegetable oils, nondrying animal oils, and mineral oils. The data reported in Table III do not warrant the conclusion that the sealing properties are definitely correlated with the drying properties, although cottonseed and linseed oils, semidrying and drying, respectively, were more effective that the nondrying oils, neat's-foot and peanut. Cottonseed oil apparently makes a very good sealing agent, judging by the satisfactory results obtained with it in this experiment and in several others of a similar nature.

TABLE III—EFFECT OF IMMERSION OF EGGS IN DIFFERENT KINDS OF OILS

IMMERSION FLUID	Method of Treatment[1]	Loss in Weight Per cent	Comparative Loss in Treated and Untreated Eggs (Untreated = 100)
At End of 5 Wks.' Storage at Room Temperature			
Cottonseed oil	I	0.5	6.3
Linseed oil	I	0.6	7.5
Neat's-foot oil	I	0.8	10.0
Peanut oil	I	1.0	12.5
Untreated	..	8.0	100.0
At End of 12 Days' Storage at 40° C.			
Mineral oil A	II	0.6	7.4
Mineral oil B	II	0.7	8.6
Mineral oil C	II	2.9	35.8
Mineral oil D	II	3.6	44.4
Untreated	..	8.1	100.0

[1] In Method I the eggs were immersed for 5 sec. in the fluid at 153° C., cooled for a few seconds in a bath of the same fluid (33° C., average), wiped gently with sterile gauze, and placed in a metal container. In Method II the eggs were immersed for 7 sec. in the fluid at 115° C., then cooled for a few seconds in a bath of the same fluid (24° to 30° C.), allowed to drain without wiping, and placed in strawboard cartons.

MINERAL OILS—The mineral oils employed in this experiment varied widely in efficiency. Mineral oil A had a specific gravity of 0.869, a flash point of 365° F., and a viscosity at 100° F. of 134 (Saybolt units). Mineral oil D had a specific gravity of 0.851, a flash point of 255° F., and a viscosity at 100° F. of 44 (Saybolt units). The other two mineral oils were intermediate in composition between A and D. The heavier oil (A) gave the best results. Equally good, and perhaps better, results might be obtained with slightly heavier oils. It is thus seen that the sealing value of these oils bears a definite relation to the grade as defined by the gravity, flash, and viscosity tests.

From the experiments thus far recorded it is apparent that a mineral oil of the type represented by mineral oil A can be used to advantage in sealing the pores of the shell of the egg. The vegetable and animal oils vary in their individual efficiency, but it seems possible to find an oil of this nature, such as cottonseed oil, which will give results comparable with those obtained with the better mineral oils. If these oils imparted an odor to the surface of the eggs, as some of them might, their use would be objectionable. Furthermore, they are more subject to change during storage than the mineral oils. In general, therefore, of the different kinds of oils of equal sealing value the mineral oils would prove the most satisfactory.

Attempts were made to increase the efficiency of the mineral oils by the addition of substances with which they are miscible. By adding about 1 or 2 per cent of soap to the four mineral oils listed in Table III it was found possible to increase their sealing properties markedly. The addition of 1 g. of soap to 100 cc. of mineral oils A, B, and D lowered the loss in treated eggs from 7.4, 8.6, and 44.4 per cent of

TABLE II—EFFECT OF IMMERSION OF EGGS IN AQUEOUS SOLUTIONS

IMMERSION FLUID	Temperature of Fluid ° C.	Duration of Immersion Sec.	METHOD OF COOLING EGGS	Loss in Weight during Storage for 18 Days at 40° C. Grams	Per cent	Comparative Loss in Treated and Untreated Eggs (Untreated = 100)
Sulfuric acid, 5 per cent	25	300	In air	1.64	2.9	26.4
Orthophosphoric acid, 3.5 per cent	25	300	In air	4.16	7.3	66.4
Trisodium phosphate, satd. soln	100	10	In immersion fluid at 30° C.	4.11	7.3	66.4
Oxalic acid, 6.5 per cent	25	300	In air	4.49	8.4	76.4
Orthophosphoric acid, 3.5 per cent	50	60	In air	5.00	9.5	86.4
Calcium acid phosphate, satd. soln	97	10	In immersion fluid at 30° C.	5.67	9.5	86.4
Sodium aluminate, satd. soln	100	10	In immersion fluid at 30° C.	5.86	9.6	87.3
Acetic acid, 6.0 per cent	25	300	In air	5.74	9.9	90.0
Acetic acid, 6.0 per cent	40	60	In air	5.01	10.1	91.8
Soap, 6.0 per cent	98	10	In air	6.56	10.7	97.3
Dipotassium phosphate, satd. soln	100	10	In immersion fluid at 30° C.	6.49	11.7	106.4
Untreated	...	..	....	6.04	11.0	100.0

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[6] The soap used in this test and throughout the investigation was a variety of ordinary, moderate priced toilet soap, white, unscented, and lighter than water.

that observed in untreated eggs to 6.2, 3.7, and 14.8 per cent, respectively. Two grams of soap added to 100 cc. of mineral oil C lowered the loss from 35.8 to 6.2 per cent. It is thus evident that soap will effectively close the pores if it is applied in a suitable medium. Attempts to raise the value of mineral oil A by additions of gums, waxes, and rosin were not successful. The results, as shown in Table IV, indicate that nothing is to be gained by such modifications when applied to relatively heavy mineral oils similar to that used in the test.

The temperatures of storage used in this investigation are much higher than those employed for the cold storage of eggs, the object being to produce a maximum effect in a comparatively short period of time. The methods which were here found to be useful in retarding shrinkage can be applied to the study of the origin of the characteristic odor and flavor which develop in eggs during cold storage.

TABLE IV—EFFECT OF VARIOUS GUMS, WAXES, AND ROSIN ON THE EFFICIENCY OF A HEAVY MINERAL OIL IN PREVENTING SHRINKAGE IN EGGS

IMMERSION FLUID[1]	Loss in Weight during Storage for 12 Days at 40° C. Grams	Per cent	Comparative Loss in Treated and Untreated Eggs (Untreated - 100)
Mineral oil A	0.20	0.4	4.0
100 cc. mineral oil A plus:			
1 g. gum guaiac	0.19	0.4	4.0
2 g. gum mastic	0.20	0.4	4.0
4 g. spermaceti	0.24	0.4	4.0
4 g. beeswax	0.26	0.4	4.0
4 g. spermaceti + 1 g. gum damar	0.26	0.5	5.0
4 g. beeswax +1 g. gum damar	0.30	0.5	5.0
1 g. gum damar	0.30	0.6	5.9
4 g. beeswax+1 g. rosin	0.36	0.7	6.9
Untreated	3.11	10.1	100.0

[1] The eggs were treated by Method II (footnote, Table III).

Method for Determining Hydrogen Sulfide Evolved by Foods when Cooked at Various Temperatures[1]

Its Application to Steam Distillation under Pressure

By **Edward E. Kohman**

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The following paper describes a method for the accurate determination of the hydrogen sulfide evolved when foods are cooked at 100° C. or higher. It involves the distillation of the sample with steam under pressure, and the gravimetric determination of the sulfide as barium sulfate.

Green corn, which was the food product used in the experiments, gives considerable quantities of substances other than hydrogen sulfide which reduce potassium permanganate, and this method makes a study of these products possible.

It is further suggested that the method and apparatus described in this paper may be applicable in the separation of many organic mixtures, or in distillations such as are involved in the determination of volatile fatty acids, where uniform amounts of distillate in a given time are desired.

In the study of the black discoloration due to the formation of ferrous sulfide which occurs in the air space of canned corn and of lye hominy, as well as in the grains of the latter, it was desirable to know the amounts of hydrogen sulfide formed during the processing of these products. A very satisfactory method has been devised, of such general application that it may be used at any temperature and for any volatile product which permits of steam distillation.

The food product to be heated is placed in a 3-l. flask, which is set in an upright autoclave or retort, supplied with steam from a boiler. (Fig. 1.) Since cork contracts in steam at high temperatures, the flask is fitted with a pine wood stopper, *c*, which contains two holes fitted with glass tubes, *a* and *b*. Tube *a* extends below the stopper to the bottom of the flask and terminates just above the stopper with a right-angled bend. This bend prevents any water which may condense on the under surface of the cover of the retort from dripping into the tube. The tube opens into the retort; therefore steam surrounding the flask enters it as the pressure is relieved by a stopcock on the other tube. Tube *b* terminates just below the stopper and extends above through the cover of the retort. It should be long enough so that the flask can be put in position before the cover is completely down. Outside the retort, this tube enters a Kjeldahl connecting bulb and then is bent to an angle of about 75°, and to it is sealed a glass tube with a stopcock. Condenser *g*, which leads to a bromine solution, follows. The steam is turned on rather rapidly when heating is begun, but the cover is not clamped down tightly until after about half a minute, so as to allow the air to escape from the retort. By means of this apparatus a temperature of 120° C. can be attained in 2 min., and the distillate can be regulated at will, while the amount of water in the flask remains constant. It was planned to collect about 650 cc. during a 45-min. distillation period at 120° C.

At the end of the distillation, the retort should be opened as soon as the pressure is relieved; otherwise the suction produced will draw the liquor out of the flask. The sulfur is determined gravimetrically as barium sulfate.

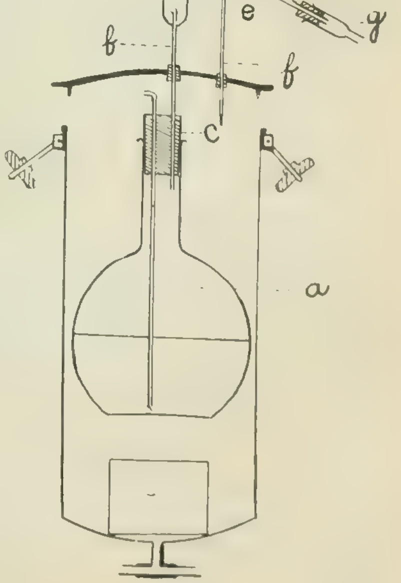

Fig. 1

One further improvement is suggested. When the steam is turned on rapidly in the retort, the cover is not clamped down until most of the air has been allowed to escape. But the air in the flask must escape through the outlet tube. If the expansion of the air is greater than can be relieved by the outlet, the back pressure may force the liquor out of the

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[1] Received January 18, 1922. Presented before the Division of Agricultural and Food Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

flask through the inlet tube. Consequently, the stopcock on the outlet tube must always be opened wide for a few seconds and gradually closed as the temperature comes up. This need of regulating each time causes a little variation in the distillate. Where it is essential to have an exact and more uniform amount of distillate, it can be obtained by using a 2-way outlet; one branch, *d* in the figure, is a large tube with a stopcock; the other, *e*, is a capillary tube of the desired diameter. Both should enter the condenser. With this arrangement, the amount of distillate will vary only with the different temperatures in the retort. In distillations like that involved in the determination of volatile fatty acids, where uniform amounts in a given time are desired, this method should prove very accurate, for the temperature of a retort supplied with steam from a boiler can be exactly regulated, to a degree not possible with the Bunsen burner or hot plate.

After the work recorded in this paper was completed, an article by Masters and Garbutt[2] was noticed, in which different attempts to determine the hydrogen sulfide formed in cooking foods are described. These authors conclude:

> It appears hardly possible to obtain a reliable measure of the amount of hydrogen sulfide produced during cooking, but it was thought that if some method, which did not involve a distillation process, could be devised, it might be possible to obtain a measure of the amount of sulfide left in the cooking water at the end of the experiment and that if all experiments were carried out under the same conditions such information might be of value for comparative purposes, even though it did not represent the total amount of sulfide produced during cooking. For this purpose a modification of the method described by Wimpler[3] was adopted, and was found to give more consistent results than the methods previously described.

The modified method which they finally adopted was to cook 100 g. of the vegetable in 750 cc. of water with a reflux condenser for 1 hr., knowing that some hydrogen sulfide was escaping and some was undergoing decomposition. Carbon dioxide was then bubbled through a measured amount of the cooking water and passed through a hydrogen peroxide solution. The hydrogen sulfide was oxidized to sulfuric acid, which was titrated with 0.01 *N* sodium hydroxide.

The method described in the present paper meets the requirements of a distillation process, described by Masters and Garbutt as "hardly possible." Air does not have access to the cooking food to cause decomposition of the hydrogen sulfide, which is carried off as it is formed, by a rapid current of steam. Masters and Garbutt observed that the distillate from foods contained acids other than hydrogen sulfide; these, however, do not interfere when the sulfur is determined gravimetrically as barium sulfate. The method is applicable at all temperatures above 100° C. and should be useful in a variety of cases. It will make possible a study of other volatile products evolved in the cooking of foods.

STEAM DISTILLATION UNDER PRESSURE

In the separation of many organic mixtures, a steam distillation process at elevated temperatures ought frequently to be applicable when the usual steam distillation at atmospheric or reduced pressure is of little or no value. As an illustration, the effect of such elevated temperatures in distilling the immiscible liquids, water and mercury, is given in Table I. The amount of mercury in the distillate was calculated from the vapor pressures by means of Avogadro's Law. Since the gram molecular volume varies directly, and in the same proportion, as the vapor pressure, we may formulate the equation

$$\frac{\text{Wt. of Hg in distillate}}{\text{Wt. of H}_2\text{O in distillate}} = \frac{200 \times \text{vapor pressure of Hg at T}^\circ}{18 \times \text{vapor pressure of H}_2\text{O at T}^\circ}$$

TABLE I

Temperature of distillation, ° C.	100	120	150	200	230
Hg in distillate, g. per l. H_2O	3.9	5.4	8.3	16.2	22.8

In Table II are given similar figures for some organic compounds. It is evident that with bromobenzene and chlorobenzene the distillation would be better carried out at 100° C., but the reverse is true for iodobenzene. Assuming for the purpose of illustration a mixture of these three compounds to be immiscible in water and in each other, a steam distillation at the lower temperature would concentrate the chlorobenzene in the distillate, whereas at the higher temperature it would concentrate the iodobenzene in the distillate. Since these three compounds are not immiscible in one another, it cannot be predicted what would happen if such a mixture were subjected to steam distillation at various temperatures. Although distillation under reduced pressures is frequently applied, distillation under pressure is scarcely considered. In many cases the possibilities of decomposition make the lower temperatures necessary. But the lack of a simple method of distillation under pressure is undoubtedly a factor in its not being used. An application of this method to some organic mixtures is certain of some interesting results. Many separations that are not successful by present methods might be effected. Tarry masses will often yield more products and no doubt in some cases products which would otherwise be lost.

TABLE II—STEAM DISTILLATION OF ORGANIC COMPOUNDS

Temperature of distillation, ° C	100	120	150	200	230
C_6H_5I in distillate, g. per l. H_2O	750	810	870	960	1000
C_6H_5Br in distillate, g. per l. H_2O	1620	1610	1580	1540	1530
C_6H_5Cl in distillate, g. per l. H_2O	2410	2280	2100	1880	1780

COOKING OF GREEN CORN

Results on 200-g. samples of lye hominy in 300 cc. of water are given elsewhere.[4] In Table III are the results obtained by cooking 1000 g. of fresh corn in the canning stage in 500 cc. of water and collecting the distillate in half-hour periods.

TABLE III—HYDROGEN SULFIDE EVOLVED WHEN GREEN CORN IS COOKED AT VARIOUS TEMPERATURES

SAMPLE No.	TEMP. ° C.	MG. SULFUR PER 1000 G. CORN, IN 0.5-HR. PERIODS							
		1st	2nd	3rd	4th	5th	6th	7th	8th
1	121	6.40	4.53	1.40	1.28	1.10	0.99	...	0.58
2	121	8.83	5.02	1.81	1.75	1.62	1.14	1.60	0.82
3	110	5.28	3.50	1.97	...	...	...	...	...
4	115	6.58	4.22	2.60	1.83	1.74	1.51	1.35	1.14
5	105	3.90	3.20	1.98	...	1.29	1.11	1.03	0.85
6	100	2.91	2.34	1.88	1.43	1.28	1.14	0.91	0.91
7	103	3.19	3.12	1.80	1.50	1.00	1.17	1.02	1.07
8	122	8.12	6.53	3.78	2.94	2.06	1.84	1.02	0.83
9	103	2.57	2.36	1.36	0.96	0.71	0.74	0.60	0.52
10	103	1.72	1.29	0.88	0.55	0.54	0.49	0.47	0.49
11	103	1.02	0.71	0.49	0.58	0.47	0.36	0.36	0.49

Samples 1 and 2 are different lots of corn and show that the amount of hydrogen sulfide evolved varies considerably for different lots of corn. Samples 2 and 3 are the same ears, one end of the ears being used for one and the other end for the other sample. The butts and tips of the ears were apportioned equally between them. By comparing the two the effect of temperature is noted. Samples 4, 5, and 6 are from the same ears, and Samples 5 and 6 are the same corn mixed after being cut from the ears. These also show the effect of temperature. Samples 9, 10, and 11 are all from the same sample of corn, cut from the cob and mixed before dividing it between the three. Sample 10, however, was given a 40-min. process at 250° F. and Sample 11 an 80-min. process at 250° F. in an open flask in a retort before hydrogen sulfide was determined. It is evident that the hydrogen sulfide escapes from the corn even though no current of steam is passing through. From a comparison of all the figures, it is evident that considerably more hydrogen sulfide is evolved during the first half hour than during the second and that the amount decreases for each succeeding period. Masters and Garbutt[2] state that the amount of hydrogen sulfide evolved when the heating is begun is relatively smaller than after the heating has been continued for a time. After reaching a maximum it again drops off. They do not state when this maximum is reached, but the indications are that it is merely a question of the food actually reaching the temperature of the experiment. In our work the live steam of the retort passed through the food product, whose temperature therefore came up with the retort temperature in about 2 min.

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[2] *Biochem. J.*, **14** (1920), 75.

[3] *Analyst*, **12** (1917), 26.

[4] THIS JOURNAL, **14** (1922), 415.

Table IV gives the effect of alkali and acids and of iron salts on the amount of hydrogen sulfide evolved by green corn when heated. The distillation was carried out at 110° C., and the distillate was collected in half-hour periods. For 1000 g. of green corn in the canning stage 500 cc. of water were used. If acid or alkali was added the amount of water was correspondingly reduced. When corn is cut from the cob the acidity rapidly rises, apparently as a result of enzymic activity. Sample 4 shows the effect of this rise in acidity on the evolution of hydrogen sulfide.

TABLE IV—EFFECT OF REACTION AND IRON SALTS

Sample No.	Treatment	Mg. Sulfur per 1000 G. Corn in 0.5-Hr. Periods 1st	2nd	3rd	4th
1	30 cc. 0.5 *N* H_2SO_4	4.54	3.42	1.83	1.35
	Without H_2SO_4	5.91	3.89	1.97	1.47
2	30 cc. 0.5 *N* NaOH	8.86	5.76	2.71	1.70
	Without NaOH	5.25	4.67	2.16	1.88
3	0.5 g. $FeSO_4.7H_2O$	8.36	6.12	3.88	1.42
	Without $FeSO_4.7H_2O$	7.70	5.59	...	1.97
4	Distilled as soon as cut from cob	5.95	4.79	2.55	1.67
	Distilled 3 hrs. later	4.76	3.97	2.28	1.56

Hydrogen sulfide is not the only product evolved when green corn is subjected to a distillation under pressure. More or less insoluble fatty material collects on the surface of the distillate and on the sides of the condensing tube. The distillate moreover has considerable reducing action toward potassium permanganate. According to the equation

$$3H_2SO_4 + 2KMnO_4 + 5H_2S = 5S + 2MnSO_4 + K_2SO_4 + 8H_2O$$

potassium permanganate is equivalent to approximately one-half its weight of sulfur in the form of hydrogen sulfide. Table V gives the amount of potassium permanganate reduced by the distillate collected in half-hour periods when 1000 g. of corn in 500 cc. of water were distilled at 110° C. and also the amount of hydrogen sulfide evolved by Sample 2. Table VI gives similar figures for variable conditions.

TABLE V—REDUCING SUBSTANCES EVOLVED BY GREEN CORN

Sample No.	Mg. KMnO Reduced by Distillate from 1000 G. Corn in 0.5-Hr. Periods 1st	2nd	3rd	4th
1	124	82	70	54
2	158	93	76	64
	Mg. Sulfur Evolved as Hydrogen Sulfide			
2	6.75	5.08	2.57	1.50

TABLE VI

Sample No.	Temperature ° C.	Time of Distillation Hrs.	Amt. of Distillate Cc.	$KMnO_4$ Reduced Mg.	Sulfur Obtained Mg.
1	110	1.33	1000	320	15.2
2	122	1.33	1500	408	16.0
3	120	1.33	1500	290	14.6

Since potassium permanganate is equivalent to about one-half its weight of sulfur, the hydrogen sulfide accounts for only about one-tenth of the reducing substance in the distillate. In the study of the discoloration of canned corn it was observed that corn which was given a high precook before canning behaved, after storage in the can, as though it had lost its reducing effect toward the container. The above figures are a confirmation of this observation.

Chemists and the Patent Laws

The Chemical Age (London) of March 25, 1922, contains extracts from a lecture by Mr. Horatio Ballantyne, which contains some advice which may be of value to American chemists. He says:

> 1—Try to ascertain, with scrupulous care, all the factors necessary for the successful performance of the invention, and, having done so, give in the specification full and clear information, illustrated by definite examples. I cannot too strongly press this counsel upon your consideration. A very large part of the costly litigation which has occurred in connection with chemical patents in the past has been due to "insufficiency" of this sort. I am happy to say that, so far as my experience goes, such faults are almost unknown in the specifications of British inventors. No doubt the defect, when it occurs, is to some extent due to the differences which exist in the requirements of the patent laws of different countries; but whatever the cause, the defect is a serious one from our own standpoint. The bargain between the Crown and the patentee requires that the informed public—in this case, competent chemists, skilled in the particular art—shall be placed by the specification in full possession of all the knowledge requisite for successfully using the invention, and anything short of a full disclosure not only imperils the validity of the patent, but is obviously unfair to the public. A "full disclosure" does not mean a dissertation on the subject; but it is better to furnish your patent agent with a lengthy description, from which he may select the essentials, than to run any risk of failure in this respect.
>
> 2—Avoid the introduction of theory into your specification, unless the circumstances are very special and your patent agent considers it necessary—and in the latter case make plain that it *is* theory. The temptation to resort to theoretical conceptions in elucidating chemical inventions is sometimes very great; none but a chemist can appreciate how helpful, as a real, practical guide, chemical theory can be and generally is. Your invention, as formulated under the sagacious advice of your patent agent, may at first sight appear rather bare. You have been contemplating, perhaps, not only particular substances, but groups of whole classes of compounds; not reactions applicable only to a few, but general reactions such as your studies and experience have familiarized you with. Your patent agent sees, lurking in such broad ideas, the danger that the claims may extend to substances or to conditions of working which result in failure. There are cases, especially in the domain of organic chemistry, where it is almost impossible to avoid theory; it is then all the more necessary to seek the aid of a patent agent who has an adequate knowledge of chemistry to guide you.
>
> 3—Do not overstate what the invention can accomplish. Nearly all inventors are enthusiasts, who do not relish seeing their inventions stated in modest terms. Now, if an invention consists in a process or apparatus, it is plain that no laudatory expressions can assist in describing that process or apparatus. Commonly it is an advantage to indicate what the object of the invention is; sometimes, but more rarely, it is advantageous to indicate what the invention is claimed in fact to achieve. Any such expressions, however, should be inserted only with the concurrence of your patent agent.

Chemical Exposition at Union College

The Union College Chemical Society held a Chemical Exposition on April 6 to 8, 1922, which contained exhibits from over fifty companies, and was attended by between seven and eight hundred people. Many of the exhibits had appeared at the Chemical Exposition in New York last September.

In addition to the exhibits, a feature which attracted a large attendance was the motion picture films illustrating various chemical industries. Two lectures also attracted a large attendance: the first by Dr. Edward Ellery on "The Chemistry of Everyday Life," and the other by Dr. Saul Dushman, on "The Structure of the Atom."

The list of American Research Chemicals, first issued as *Circular* 23 of the National Research Council has been revised, and is expected to be ready for distribution about June 1. The revised list contains the products of eighty-two manufacturers. It follows the general scheme of the earlier list, but contains in addition a list of vital stains. Copies can be secured from the Research Information Service, National Research Council, Washington, D. C.

The Composition of Soy-Bean Oil[1]

By W. B. Smith[2]

Armour & Co., Kansas City, Kansas

Very little seems to have been published regarding the composition of soy-bean oil, although many data concerning its "constants" have appeared in the last few years. Matthes and Dahle's[3] statement that the fatty acids consist of 15 per cent palmitic, 56 per cent oleic, 19 per cent linolic, and 5 per cent linolenic acids, has been quoted recently, but as the iodine number of such a mixture is 99, while soy-bean oil has an iodine number around 130, it is evident that this is not the correct composition.

The principal reason for the discrepancy lies in the fact pointed out by Jamieson and Baughman,[4] that a large proportion of the linolic tetrabromides of some oils remains in solution in the mixture of oleic dibromide and petroleum ether. When this fact is recognized, the correlation of the analysis of the unsaturated acids with the known constants becomes simplified. Some of the chief constants which have been published are the following:

	Fellers[1]	Matthes and Dahle[2]	Oettinger and Buchta[3]	Low[4]	Bailey and Baldsiefen[5]	Lewkowitsch[2]	Twitchell[6]	Steele and Washburn[7]
INDEX OF REFRACTION								
Maximum	1.4750(25°)	1.4680(40°)	1.4755(20°)	..	..	..	..	..
Minimum	1.4720	....	1.4745	..	..	..	..	..
IODINE NUMBER								
Maximum	132.3	....	....	138.4 (Wijs)	135.5	..	..	..
Minimum	123.2	....	....	137.4	133.2	..	..	..
SAPONIFICATION NUMBER								
Maximum	195.8	....	....	..	..	192.5	..	..
Minimum	190.2	....	....	..	..	190.6	..	..
INSOLUBLE ACIDS AND UNSAPONIFIABLE MATTER								
Maximum	94.3	95.5	96.0	96.1	..	..	..	..
Minimum	93.0	....	95.8	..	..	..	..	..
UNSAPONIFIABLE MATTER (PER CENT)								
Maximum	....	....	0.59	1.16	..	..	..	..
Minimum	....	....	0.39	..		..	..	..
REICHERT-MEISSL NUMBER								
Maximum	5.2	....	0.56	..	..	..	..	..
Minimum	4.3	....	0.45	..	..	..	..	..
SOLID ACIDS (PER CENT)								
Maximum	9.2	....	....	..	..	..	17.01	..
Minimum	8.6	....	....	..	..	..	..	..
LIQUID ACIDS (PER CENT)								
Maximum	85.7	....	....	..	..	..	..	..
Minimum	84.9	....	....	..	..	..	..	..
HEXABROMIDES (PER CENT)								
Maximum	....	....	....	..	7.5	7.78	..	2.2
Minimum	....	....	....	..	4.2	5.07	..	..
Average	....	....	....	..	6.0	..	..	..

[1] This Journal, **13** (1921), 689.

[2] Lewkowitsch, "Oils, Fats, and Waxes," 5th edition, II, 116; I, 575.

[3] *Z. angew. Chem.*, **1911**, 24, 828.

[4] This Journal, **12** (1920), 572.

[5] *Ibid.*, **12** (1920), 1193.

[6] *Ibid.*, **13** (1921), 807.

[7] *Ibid.*, **12** (1920), 59.

Experimental

Analyses bearing on the subject have been made on four samples of soy-bean oil, representing four different sources as well as more than ten years' time. Standard methods were employed in every case, more than ordinary care being observed.

	1	2	3	4
Specific gravity 15.6°/15.6°.	....	....	0.9249	0.9245
Index of refraction, 25° C....	1.4741	1.4734	1.4732	1.4734
Iodine number (Hanus)......	134.0	133.1	129.4	132.[illegible]
Free fatty acids, per cent.....	0.8	....	....	....
Insoluble acids + unsaponifiable, per cent..............	95.3	....	....	....
Soluble acids, per cent........	0.3	....	....	....
Unsaponifiable matter, per cent	1.0	....	....	....
Solid acids, per cent..........	9.7	7.74	11.6	9.60
Iodine number................	5.7	5.0	....	7.4
Melting point................	53.5	52.5	....	53.4
Molecular weight.............	274.	271.	....	....
Liquid acids, per cent.........	85.5	....	83.5	....
Iodine number................	....	151.7	....	154.4
Hexabromides (m. p. 181°), per cent...................	6.55	7.23	....	....
Linolenic acid, per cent......	2.40	2.60	....	....

These analyses average 9.7 per cent of solid acids, with an average iodine number of 6. Taking the iodine value of the unsaturated acids as 153, the solid acids contain about 4 per cent of unsaturated acids, so that the percentage of saturated acids when corrected for this becomes 9.3. This result is very close to that of Fellers.[5] Owing to the small quantities of solid acids recovered, tests of their character were inconclusive. According to Matthes and Dahle,[3] palmitic acid is the only saturated acid present.

The percentage of linolenic acid in soy-bean oil appears to have been well worked out. Excluding Steele and Washburn's result,[6] which is much lower than the others, the limits are from 4.2 to 7.8 per cent of hexabromide, corresponding to 1.54 to 2.86 per cent of linolenic acid. Bailey and Baldsiefen found the average of hexabromides to be 6.0, equivalent to 2.2 per cent of linolenic acid. The average of 2.5 per cent found experimentally agrees with these figures.

The palmitic and linolenic acids account for less than 12 per cent of the oil, which must contain a large proportion of linolic acid. To determine this, Oil 1 was tested in the manner described by Jamieson and Baughman.[4] The filtrate from the hexabromide determination was freed from ether

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[1] Received January 13, 1922.

[2] Chemist, Armour & Co.

[3] Lewkowitsch, "Oils, Fats, and Waxes," 5th edition, II, 116; I, 575.

[4] *J. Am. Chem. Soc.*, **42** (1920), 1199.

[5] This Journal, **13** (1921), 689.

[6] *Ibid.*, **12** (1920), 59.

by boiling (after removing the excess of bromine with thiosulfate and drying), dissolved in petroleum ether, and the linolic tetrabromides allowed to crystallize in the ice box. The next day these were filtered, washed, and dried. The filtrate was dried and weighed, and the percentage of bromine was determined. From these results the amounts of linolic and oleic acid were calculated.

	Grams	Per cent
Weight of unsaturated acids	5.000	...
Linolenic hexabromide, m. p. 181°	0.3830	7.66
Linolenic acid	....	2.81
Insoluble tetrabromide, m. p. 112°	1.7560	35.12
Residue (tetrabromide and dibromide)	7.7350	...
Bromine content of residue	....	47.96
Tetrabromide in residue	5.3139	...
Dibromide in residue	2.4211	....
Linolic acid in residue	2.4800	49.60
Linolic acid in insoluble tetrabromide	....	16.39
Total linolic acid	....	65.99
Oleic acid	1.5451	30.90

These figures show the following composition of the unsaturated acids and the original oil:

	Unsaturated Acids Per cent	Original Oil as Found Per cent	Original Oil Corrected Per cent
Linolenic acid	2.81	2.4	2.4
Linolic acid	65.99	56.4	56.6
Oleic acid	30.90	26.4	26.5
Solid acids	...	9.7	9.3
TOTAL	99.70	94.9	94.8

The figures in the last column were obtained by deducting 0.36 per cent of unsaturated acids from the solid acids as found, and correcting the percentages of unsaturated acids accordingly. The iodine value of the above mixture is theoretically 155 for the unsaturated acids, and 133.0 for the original oil, while 153 and 134.0 are values found on experiment (the value 153 is the average of two other samples).

From the data obtained it is believed that the composition of soy-bean oil having an iodine number of 134 is approximately as follows: 2 to 3 per cent linolenic, 55 to 57 per cent linolic, 26 to 27 per cent oleic, and 9 to 10 per cent saturated acids.

Glacial Acetic Acid Method for Determining Uranium in Carnotite[1]

By **Wilfred W. Scott**[2]

Department of Chemistry, Colorado School of Mines, Golden, Colorado

THE growing demand for radium has been an incentive to an increased interest in certain radium bearing minerals, the most important of which is carnotite.[3] Since there appears to be a definite ratio of radium to uranium in the ore, the uranium content is an approximate measure of the amount of radium present,[4] so that a rapid method for the determination of uranium is much to be desired.

The usual accompanying substances in carnotite are silica, iron, aluminium, and vanadium, and the method should provide for the separation of uranium from these elements.

Carnotite is easily decomposed by mineral acids. The procedure commonly employed is to treat the ore with nitric acid at boiling temperature (adding sulfuric acid if decomposition by the nitric acid is incomplete), filter off the silica, precipitate iron and alumina as carbonates with an excess of ammonium carbonate, precipitate vanadium from a slightly acetic acid solution as lead vanadate, remove the excess of lead either as a carbonate and sulfide, or as sulfate, and determine uranium by precipitation with ammonia, ignition to U_3O_8 and weighing as impure oxide. The residue is extracted with nitric acid, and the weight of insoluble residue is subtracted from the weight obtained, to arrive at the true U_3O_8. The method is long and requires some experience for accurate results.

W. F. Hillebrand suggests separating vanadium from uranium by volatilization of the former as the oxychloride with hydrochloric acid gas. The method is not popular in the industrial laboratory on account of the apparatus required.

C. E. Scholl[5] has outlined a rapid method which in part follows the procedure recommended by the Bureau of Mines[6] for the commercial separation of the constituents of carnotite. Scholl, however, separates the vanadium in the initial carbonate treatment to remove iron and aluminium by adding sufficient iron in excess of that present to carry out the vanadium. Unfortunately the vanadium is not completely removed and may often be found in the final residue U_3O_8; furthermore some uranium is invariably carried down by the iron and aluminium.

C. A. Pierlé[7] has shown that vanadium may be quantitatively separated from uranium by extracting the nitrates with glacial acetic acid containing nitric acid in the proportion of 100:5. The uranium dissolves while the vanadium remains in the residue. After investigating the reaction the writer conceived the idea of using this principle in a quantitative method for the determination of uranium in carnotite.

Attempts were first made to extract the ore directly, with unsatisfactory results; roasting the ore before treating with the glacial acetic nitric mix proved more effective and indicated a commercial possibility. The best results were obtained by decomposing the ore with dilute nitric acid, filtering off the soluble constituents containing all of the uranium and evaporating to dryness, or treating the ore with nitric acid and evaporating to dryness without separating the silica, thus saving a filtration. The residue thus obtained was extracted with the glacial acetic-nitric reagent.

It was found necessary to evaporate the extract to dryness and reëxtract the uranium to effect a complete separation of uranium from vanadium (see experimental data). A final evaporation to dryness and ignition to destroy organic matter appears necessary for a complete precipitation of uranium. Pyrex glass has been found to be satisfactory.

PROCEDURE

Half a gram (100 mesh) of high-grade carnotite, or a larger amount of low-grade, is placed in a 300- to 400-cc. beaker and treated with 20 to 40 cc. dilute HNO_3 (1:1) and the mixture boiled gently and placed on a steam bath or hot plate over an asbestos mat to keep hot until the decomposition is complete and only white silica remains.[8] The solution is now rapidly evaporated to dryness, the beaker being covered by a watch glass mounted on glass riders to lessen condensation. The residue is baked for a few minutes to expel water.

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[1] Received January 12, 1922.

[2] Associate Professor of Chemistry, Colorado School of Mines.

[3] *Am. J. Sci.*, [4] **10** (1900), 120; *U. S. Geol. Surv., Bulls.* **70, 104, 625.**

[4] 2.6 times per cent of U_3O_8 gives mg. radium per ton. Ratio U : Ra = 1 : 3.4×10^{-7}. S. C. Lind and L. D. Roberts, *J. Am. Chem. Soc.*, **42** (1920), 1170.

[5] THIS JOURNAL, **11** (1919), 842.

[6] *Bur. Mines, Bull.* **104.**

[7] THIS JOURNAL, **12** (1920), 61.

Twenty-five cc. of glacial acetic-nitric acid mixture (100 : 5) are added, and the sides of the beaker and the watch glass are rinsed down to remove any adhering residue, by means of a policeman if necessary. The mixture is heated to boiling and kept at boiling temperature for about 5 min. (To prevent loss of glacial acetic, a round-bottomed flask filled with cold water and placed over the beaker has been found effective. The strength of acetic to nitric must be kept in the ratio of 10 or more to 1; otherwise vanadium is appreciably attacked.)

The extract is filtered from the red residue, which contains over 95 per cent of the vanadium, practically all of the silica, and a large proportion of the alumina and iron. The beaker is rinsed out with the least amount of the glacial reagent necessary and the filter washed down with several small portions of the acid.

The extract containing all of the uranium is evaporated to dryness (in the hood), the residue baked, and ignited gently over a free flame until the residue turns black. The extraction with glacial acetic-nitric is repeated with 15 to 20 cc. of the acid, the acid being heated to near boiling. Four or five minutes are ample to effect the solution of the uranium.

The extract is filtered off as stated in the previous step and evaporated to dryness and the residue baked and ignited to destroy the organic matter, which would interfere with the precipitation of uranium.

The black residue is dissolved in 10 cc. nitric acid and 40 cc. of water, warming if necessary. The free acid is partly neutralized with ammonium hydroxide, the beaker is covered, and solid ammonium carbonate is added in sufficient excess to dissolve the carbonate of uranium that first precipitates. The addition of the carbonate effects precipitation of iron and alumina that remain in the solution. From 2 to 3 g. more of ammonium carbonate are added and 5 cc. of ammonium hydroxide. The solution is now filtered from the precipitate, and the residue washed with hot water.

The filtrate containing uranium is acidified with nitric acid which is added through the lip of the beaker, the beaker being covered to prevent loss by effervescence. A precipitate of uranium carbonate first forms and redissolves with the excess of acid. The solution is heated to boiling to expel carbon dioxide, which prevents precipitation of uranium. Ammonium hydroxide is added in decided excess and the boiling continued until the uranium precipitates completely. The supernatant solution which is obtained when the precipitate settles should be colorless. A yellowish color indicates uranium and the boiling should be continued. The addition of ammonium nitrate assists in the complete precipitation of ammonium uranate. Generally a sufficient amount is present.

The precipitate is filtered off, and the beaker is rinsed out with a little of the filtrate and the least amount of 2 per cent ammonium nitrate necessary. Washing the precipitate is not required. After drying slightly to expel most of the moisture the precipitate is ignited and weighed as U_3O_8.

The residue should dissolve completely by boiling with dilute nitric acid. If it does not, any residue remaining should be filtered off, washed free of uranium, and ignited. The weight of this residue is deducted from the oxide of uranium obtained above.

EXPERIMENTAL DATA

	SiO_2	Fe_2O_3	Al_2O_3	V_2O_5 in Two Residues from Acetic Extract	U_3O_8
Taken	0.2000	0.1430	0.0000	0.2000	0.2000
Found	0.1963	0.1416	....	0.1993	0.1992
Taken	0.4000	0.2500	0.0500	0.1000	0.2000
Found	....	....	....	0.1020	0.1988
Taken	0.1000	0.3500	0.0500	0.3000	0.2000
Found	....	....	....	0.3001	0.1997
Taken	0.2000	0.1500	0.0500	0.4000	0.2000
Found	....	....	....	0.3936	0.2004
Taken	0.2000	0.0500	0.0500	0.5000	0.2000
Found	....	....	....	0.4978	0.1996

ANALYSIS OF CARNOTITE (PER CENT U_3O_8)

	Standard Procedure	Scholl's Method	Emanation Method	New Method
a	24.93	25.05	....	25.16
b	.....	24.56	24.2	24.23

SOLUBILITY OF U_3O_8 IN 25 CC. GLACIAL-NITRIC MIX

0.2000 g. taken.	Soln. complete in 2 min. in hot reagent
0.5000 g. taken.	Soln. complete in 3 min. in hot reagent
1.0000 g. taken.	Soln. complete in 2 min. in boiling reagent
5.0000 g. taken.	4.478 g. dissolved in 5 min. in boiling reagent

SOLUBILITY OF V_2O_5 IN 25 CC. GLACIAL-NITRIC MIX

0.1000 g. taken.	0.0026 g. dissolved after 5-min. boiling
1.0000 g. taken.	0.0034 g. dissolved after 5-min. boiling

The following results were obtained by students in the analysis of carnotite. The methods are designated by the reagent used in the separation of vanadium from uranium. Results are reported in grams of U_3O_8 found.

Lead Acetate Method Grams U_3O_8	Ferric Iron Method Grams U_3O_8	Glacial Acetic Method Grams U_3O_8
	High-Grade Ore, 0.5-G. Sample	
0.1265	0.1269	0.1247
0.1247	0.1257	0.1248
0.1250	0.1268	0.1246
0.1243	0.1257	0.1255
0.1241	0.1263	0.1256
0.1245	0.1260	0.1260
0.1243	0.1265	0.1259
0.1248	0.1250	0.1243
0.1230	0.1245	0.1245
0.1232	0.1230	0.1248
0.1231	0.1238	0.1242
0.1238	0.1230	0.1245
Av. (Per cent) 24.85	25.05	24.99
	Low-Grade Ore, 5-G. Sample	
0.1265	0.1170	0.1250
0.1235	0.1210	....
0.1225	0.1365	....
....	0.1367	....
Av. (Per cent) 2.483	2.556	2.5

ACKNOWLEDGMENT

The writer wishes to thank his colleague, Professor L. D. Roberts, for his kind review of this paper.

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[8] Addition of sulfuric acid may be necessary for complete solution of uranium. Generally carnotite decomposes readily with the method given. A few drops of hydrofluoric acid hasten the decomposition.

The Chemical Situation in Italy

Dr. Riccardo Cuisa, Chemical Institute of the Royal University at Bologna, Italy, after having read the article, "Chemically Speaking, How's Europe," by Watson Davis, which appeared in the December number of THIS JOURNAL, has noted that Italy was not mentioned in this survey of chemical conditions in Europe which was based on information obtained from a number of American chemists who visited Europe last summer. He gives the following information regarding chemistry in Italy:

"The pay of the professors is going to be increased, as have already been the endowments of laboratories, and the number of students is growing.

"The chemical industry is recovering its former condition in relation to agriculture, and the lack of coal is felt everywhere. With coal, chemically speaking, Italy would be inferior to no country."

The Composition of Commercial Phosphoric Acid[1,2]

By William H. Ross, C. B. Durgin and R. M. Jones

Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

A study has been made of suitable methods for determining the inorganic constituents of commercial phosphoric acid and an outline is given of simple and accurate methods which have been devised or adapted for the purpose. The methods are also applicable to the analysis of alkali and other soluble phosphates and, with suitable modifications, to the analysis of insoluble phosphates.

Tabulated results are given showing the composition of different samples of phosphoric acid prepared from bones and from phosphate rock by the sulfuric acid method, and from phosphate rock by the volatilization method. The volatilized acids are relatively low in such nonvolatile constituents as calcium, iron, aluminium, and manganese. The presence of other elements such as lead, sulfur, chlorine, and fluorine in unrefined acids depends more on contamination and on the composition of the rock or bones from which they are obtained than on the process used in their preparation. The lowest proportion of inorganic constituents in the samples analyzed was found in a volatilized acid that had been collected in a Cottrell precipitator and commercially refined.

THE four leading mineral acids of this country, in the order of their production, are sulfuric, hydrochloric, nitric, and phosphoric. In the pre-war year of 1913 the production of sulfuric acid in terms of 50° Bé. acid amounted to 3,538,890 tons, as compared with only about 25,000 tons of phosphoric acid. The consumption of phosphoric acid is thus seen to be small as compared with sulfuric acid, but within recent years a marked increase has been noted in the demand for this acid, particularly in those industries which have to do with the preparation of food products. This is illustrated by its use in sugar refining, in fermentation, in water softening, and in the manufacture of soft drinks, baking powder, yeast, jams and jellies, hydrogen peroxide, and other medicinal preparations.

Sulfuric acid is used in a great many industries, but the bulk of this acid, amounting under normal conditions to upwards of 50 per cent of the total, is consumed in the production of a soluble salt of phosphoric acid, *viz.*, monocalcium phosphate, or superphosphate as it is more commonly known in the fertilizer trade. Monocalcium phosphate and other soluble phosphates may also be produced from phosphoric acid independently of sulfuric acid and small quantities of these salts are now being produced in this way. If this practice were to become general the production of phosphoric acid would then approach that of sulfuric acid. It is improbable that sulfuric acid will ever be entirely replaced by phosphoric acid in the manufacture of phosphatic fertilizers, but the possibilities in this direction and the many other uses for which it is now being employed emphasize the potential future importance of commercial phosphoric acid.

Two methods are now being employed for the preparation of phosphoric acid of commercial grade. The older of these methods consists in treating bones or phosphate rock with sufficient sulfuric acid to set free the phosphoric acid. The other method, which is of comparatively recent development, depends on volatilizing the acid from phosphate rock by igniting with sand and coke at a high temperature in an electric[3] or other furnace.[4] In experiments that were made some time ago by the Bureau of Soils it was found that the Cottrell precipitator[3] could be applied very effectively to the collection of the volatilized acid and this process of recovery is now in commercial use.

In the manufacture of superphosphate by the sulfuric acid process the rock is ordinarily treated with only sufficient acid to form the monocalcium phosphate. No attempt is made to separate the calcium sulfate that is formed in the reaction and the marketed product is therefore lower in phosphoric acid than the original rock from which it is prepared. Most of the other materials that are now used in fertilizers are also low grade and the practice has therefore developed of making only low-grade mixtures for use in the fertilizer trade. The use of high-grade materials under present conditions would add to the cost of manufacture, inasmuch as filler would then have to be added to make a fertilizer of desired grade. It is recognized, however, that if all the standard fertilizing elements could be obtained in concentrated form it would then be advantageous to make at least some high-grade fertilizers to supply the demand of distant markets. A source of the nitrogen for such concentrated mixtures is furnished by the fixation of nitrogen in the form of ammonia. When this is neutralized with phosphoric acid a concentrated product is obtained which contains two of the three essential constituents of a complete fertilizer. By mixing this salt with other concentrated materials, such as ammonium nitrate and potassium phosphate or sulfate, it is possible to prepare a concentrated fertilizer having any desired proportion of the fertilizing elements.

In a study of the preparation and application of concentrated fertilizers, it was found necessary as a preliminary step to develop suitable methods for the analysis of these materials and particularly of the phosphoric acid used in their preparation. It was found that the methods that are applicable to the determination of many of the constituents of phosphatic materials like phosphate rock cannot be applied to the analysis of phosphoric acid unless the latter is first neutralized with an alkaline earth base. This procedure, however, gives a very bulky precipitate which so dilutes the constituents to be determined as to increase greatly the error of analysis.

An attempt was therefore made to concentrate and separate the constituents to be analyzed from the excess of free acid by precipitation or volatilization of the former, or to determine them directly in the acid by volumetric or colorimetric methods. By applying one or the other of these procedures it was found possible to devise or adapt methods for the determination of all the ordinary constituents of phosphoric acid with the exception of the alkalies. For the analysis of these constituents it was found necessary to separate the element to be determined from the phosphoric acid by the opposite procedure of precipitating the latter.

In Table I are given results that have been obtained in the analysis of samples of phosphoric acid that have been prepared from bones and from phosphate rock by the sulfuric acid method and also of acid prepared from phosphate rock by the volatilization method. Three of the samples are of "raw" phosphoric acid, while the remaining samples repre-

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[1] Received February 28, 1922. Presented at the 37th Annual Meeting of the Association of Official Agricultural Chemists, October 24, 1921, and printed by courtesy of the *Journal* of that Association.

[2] Published by permission of the Secretary of Agriculture.

[3] W. H. Ross, J. N. Carothers and A. R. Merz, This Journal, **9** (1917), 26; J. N. Carothers, *Ibid.*, **10** (1918), 35.

[4] W. H. Waggaman and T. B. Turley, *Ibid.* **12** (1920), 646, *Chem Met. Eng.*, **23** (1920), 1057.

TABLE I—COMPOSITION OF COMMERCIAL PHOSPHORIC ACID

						CONSTITUENTS PRESENT ON BASIS OF 50 PER CENT CONCENTRATION											
SAMPLE	SOURCE	Method of Preparation	Quality	Specific Gravity	Concentration Per cent H_3PO_4	Na Per cent	K Per cent	Ca Per cent	Fe Per cent	Al Per cent	Mn Per cent	Pb P.p.m.	AS_2O_3[1] P.p.m.	Total S as H_2SO_4 Per cent	HCl Per cent	HF Per cent	Total Per cent
1	Phosphate rock	Sulfuric acid	Raw	1.4606	53.47	0.20	Trace	0.14	1.21	0.66	0.126	9	2.0	0.47	0.012	0.20	3.02
2	Phosphate rock	Sulfuric acid	Raw	1.2371	27.60	0.76	0.08	1.20	1.88	1.22	0.149	0	1.0	0.65	0.027	1.54	7.36
3	Phosphate rock	Volatilization and recovery by absorption in water	Raw	1.5428	69.99	0.13	0.04	0.04	0.18	0.27	0.004	4	1.0	0.27	0.013	0.19	1.13
4	Phosphate rock	Sulfuric acid	Refined	1.4123	55.20	0.41	0.12	Trace	0.19	0.10	0.155	7	0.75	0.46	0.044	0.05	1.53
5	Phosphate rock	Sulfuric acid	Refined	1.4221	55.12	0.35	Trace	0.16	0.34	0.23	0.348	4	1.0	0.13	0.035	0.11	1.70
6	Phosphate rock	Sulfuric acid	Refined	1.3261	39.40	0.06	0.03	0.14	1.00	1.25	0.184	14	1.0	1.25	0.012	0.96	4.89
7	Bones	Sulfuric acid	Refined	1.3805	52.27	0.16	Trace	0.20	0.50	0.11	0.014	0	2.5	0.42	0.003	0.04	1.45
8	Bones	Sulfuric acid	Refined	1.2309	32.15	0.53	Trace	1.36	0.84	0.19	0.021	9	1.0	0.28	0.023	0.14	3.39
9	Phosphate rock	Volatilization and recovery by Cottrell precipitator	Refined	1.3955	56.89	0.10	0.16	0.00	0.08	0.04	0.005	12	1.0	0.09	0.000	0.02	0.50
10	Phosphate rock	Volatilization and recovery by Cottrell precipitator	Refined	1.6310	79.50	0.12	0.18	Trace	0.17	0.06	0.004	8	0.5	0.07	0.000	0.01	0.61

[1] Analyses by R. M. Hann, Bureau of Chemistry.

sent commercial acids from different sources that have been refined or treated for the elimination of certain impurities. The concentration of the different samples varied from 27.6 to 79.5 per cent H_3PO_4. In order that the results might be comparable, the values obtained for each sample were recalculated on the basis of a common concentration of 50 per cent acid.

A comparison of the results given in Table I will show that the volatilized acids are relatively low in such nonvolatile constituents as calcium, iron, aluminium, and manganese. The lead found in the different acids no doubt arises by contamination from lead containers with which the acid comes in contact either during or after its preparation, and the amount present is therefore not characteristic of any special make of acid. The same remark also applies to the presence of sulfur. In the volatilized acids this originates from the sulfur in the coke used in smelting the rock and in the other acids from the sulfuric acid used in their preparation. Raw acid prepared from bones is relatively low in chlorine and fluorine but the content of these constituents in other unrefined acids seems to depend more on the composition of the phosphate rock used than on the process used in the preparation of the acids.

In the investigation that was made by the Bureau of Soils[3] on the volatilization and recovery of phosphoric acid it was predicted that raw acid prepared by smelting phosphate rock in an electric furnace and collecting the fumes in a Cottrell precipitator would probably be of superior quality to that prepared from phosphate rock by the sulfuric acid method. The samples listed in Table I do not represent all the plants that produce phosphoric acid in this country, and it is possible, notwithstanding the care that was taken to obtain average samples, that some of those analyzed may not be representative. The results on the whole indicate, however, that volatilized acid that has been collected in a Cottrell precipitator and treated if necessary for the removal of certain volatile impurities is at least of an equal grade of purity with any commercial acid on the market.

ACCURACY OF METHODS OF ANALYSIS

In testing and devising methods for the analysis of phosphoric acid, special efforts were made to develop methods which would not only give results of reasonable accuracy but which were also sufficiently rapid to admit of being applied in factory control work. Most of the methods that were finally adopted are thought to be sufficiently rapid to meet the latter requirement, and the accuracy of all was tested by the analysis of samples prepared by adding known amounts of salts to C. P. phosphoric acid.

Table II shows the composition of three of these synthetic samples which were prepared in imitation of the commercial samples 2, 8, and 10 in Table I. In the preparation of the samples for analysis, weighed amounts of calcium carbonate, ferric phosphate, aluminium phosphate, manganese carbonate, sodium chloride, and lead nitrate were dissolved in 100 cc. of hot phosphoric acid (1.71 sp. gr.), cooled, and made up to the mark in a 1000-cc. flask, from which aliquot portions were taken for the analysis of the constituents added. The samples were prepared by one of the authors and analyzed by the other two without previous knowledge of their composition. Blank corrections were applied when it was necessary to correct for impurities in the reagents. Lead in particular was found to occur in many C. P. chemicals. Thus, analyses of several samples of C. P. phosphoric acid obtained from different sources showed a lead content varying from 32 to 41 p. p. m., or more than was found in any of the commercial samples.

TABLE II—ANALYSES OF PREPARED SAMPLES OF 50 PER CENT PHOSPHORIC ACID

(Results expressed in percentages, except in case of lead, which is in p. p. m.)

	SAMPLE 1		SAMPLE 2		SAMPLE 3	
CONSTITUENTS	Added	Found	Added	Found	Added	Found
Calcium, Ca	1.20	1.21	1.40	1.43	0.05	0.05
Iron, Fe	2.00	2.03	0.75	0.79	0.20	0.22
Aluminium, Al[1]	1.20	1.27	0.20	0.21	0.05	0.043
Aluminium, Al[2]	1.20	1.25	0.20	0.22	0.05	0.047
Manganese, Mn	0.15	0.14	0.020	0.023	0.004	0.005
Hydrogen chloride, HCl	0.030	0.029	0.020	0.021	0.0	0.0
Lead, Pb	0.0	0.5	75	72	10	11

[1] Iron and aluminium separated with sodium hydroxide.

[2] Iron and aluminium separated with sodium thiosulfate and ammonium acetate.

METHODS OF ANALYSIS

An outline of the methods used in the analysis of the samples listed in Tables I and II is as follows:

PREPARATION OF SAMPLE

Weigh from 100 to 400 g. of the acid, depending on its concentration and purity, into a 1000-cc. flask, dilute with water, warm if necessary until the solution becomes clear, cool, and make up to the mark. Designate this as Solution A.

SODIUM AND POTASSIUM

Transfer an aliquot portion of Solution A, containing about 5 g. of the acid, to a 250-cc. flask. Make alkaline with ammonia as indicated with litmus, heat to boiling, add sufficient calcium chloride in solution to precipitate all the phosphate, cool, make up to the mark, allow to settle, and determine sodium and potassium in an aliquot part of the clear solution by the platinum chloride method in the usual way.

Calcium

Transfer an aliquot part of Solution A, containing 5 to 20 g. of the acid, into a 250-cc. beaker, add 10 cc. of sulfuric acid (1 : 4), dilute to 50 cc., add 150 cc. of 95 per cent ethyl alcohol or methanol and allow to stand until the precipitate has settled.[6] Filter, wash with 50 per cent alcohol, transfer precipitate and filter paper to a 150-cc. beaker, dissolve the precipitate in hot dilute hydrochloric acid, make alkaline with ammonia, acidify again with 30 per cent acetic acid using a few cc. in excess, precipitate calcium with ammonium oxalate in the usual way, filter, wash, ignite to CaO, and weigh.

A method that is frequently recommended for the determination of calcium in phosphate rock by precipitating as the oxalate in the presence of iron and aluminium in citric acid solution was found to give unsatisfactory results when applied to the analysis of phosphoric acid.

Iron

Transfer an aliquot part of Solution A, containing 5 to 10 g. of the acid, to a 250-cc. beaker, dilute to about 200 cc., add 15 cc. sulfuric acid (1 : 4), pass through a Jones reductor and determine the iron in the usual way by titrating with standard potassium permanganate solution.

Aluminium

Transfer an aliquot part of Solution A, containing 2 to 10 g. of acid, to a 250-cc. beaker. Add sufficient calcium as calcium chloride to make the diphosphate and about 10 per cent in excess. Dilute to about 200 cc., heat to boiling, and pour slowly with stirring into a 500-cc. flask containing a hot 10 per cent solution of sodium hydroxide of sufficient volume to make the mixture strongly alkaline.[7] Cool, make up to the mark, allow to settle, or filter and transfer an aliquot part of the clear solution to a 400-cc. beaker; acidify with dilute hydrochloric acid (1 : 4), using the minimum amount necessary to dissolve the precipitate that forms during the addition of the acid. Heat to boiling, add 1 g. of sodium thiosulfate in solution, boil for about 20 min., add 15 cc. of a 50 per cent ammonium acetate solution containing 5 cc. of glacial acetic acid,[8] boil for about 5 min. longer, filter hot, wash, ignite, and weigh as $AlPO_4$.

The aluminium in phosphoric acid may also be determined as follows:

Transfer an aliquot portion of Solution A, containing 2 to 10 g. of acid, to a 600-cc. beaker, dilute to about 400 cc., heat to near boiling, add ammonia if necessary until a permanent precipitate forms, and clear with the minimum quantity of dilute hydrochloric acid. Add 2 to 10 g. of sodium thiosulfate,[9] depending on the amount of aluminium present, boil for about 20 min. and precipitate aluminium with ammonium acetate and acetic acid as in the preceding method. On filtering, transfer the filter paper containing the precipitate to the same beaker, dissolve in a little hot hydrochloric acid, dilute to about 300 cc., heat to near boiling, adjust the acidity as before the first precipitation, add a little sodium thiosulfate in solution, boil, and reprecipitate as before. Filter, wash, ignite, and weigh as $AlPO_4$.

Unless carried out properly this method is likely to carry down iron and manganese along with the aluminium, and it makes no provision for the removal of such elements as titanium and zirconium, if present. It is therefore not as satisfactory a method as the one first described.

Manganese

Transfer an aliquot part of Solution A, containing 5 to 10 g. of the acid, to a 100-cc. flask, dilute with water, add 20 cc. of concentrated nitric acid, heat to boiling and add sufficient of a 1 per cent silver nitrate solution to precipitate all the chlorine, using an excess of about 3 cc., boil until the precipitate coagulates, cool, make up to the mark, transfer an aliquot portion of the clear solution to a 150-cc. beaker, dilute to 100 cc., heat to 80°, add 1 to 2 g. of ammonium persulfate,[10] stir, and allow to settle until cool. Place in a 100-cc. Nessler tube and match the color in a Hurley-Kennicott colorimeter with a standard potassium permanganate of a stronger color than the solution analyzed but not more than five times as strong. Standard permanganate solutions of 0.01 *N* and 0.001 *N* will usually be found to furnish a sufficient range of color. When the colors are matched, the manganese per cc. of the standard solution used, multiplied by the reading of the tube containing the standard solution, gives the manganese in the aliquot portion of the solution taken for analysis. If too much or too little silver nitrate is used in this determination the permanganate color will not develop properly and it is therefore important that the directions given for the use of this reagent be followed rather closely.

Lead

Transfer an aliquot part of Solution A, containing 5 to 15 g. of acid, to a 250-cc. beaker, add 10 cc. of sulfuric acid (1 : 4), and about 1 g. of calcium sulfate in the form of a paste. Precipitate calcium and lead as in the Chittick[11] method for determining lead in baking powder by the addition of sufficient 95 per cent alcohol (ethyl or methyl) to make a 70 per cent solution. Let stand until the precipitate begins to settle, filter, and wash with 70 per cent alcohol. Transfer filter paper and precipitate to a 150-cc. beaker, add 50 cc. of an alkaline ammonium acetate solution prepared by diluting one volume of ammonium hydroxide (sp. gr. 0.90) with an equal volume of water and then pouring into two volumes of 35 per cent acetic acid. Boil for a few minutes, decant through a filter into a 200-cc. flask, digest the residue again with a fresh portion of the ammonium acetate solution, and repeat a third time or until the greater portion of the calcium sulfate has been dissolved. Cool the combined filtrates, acidify with acetic acid, make up to the mark, transfer an aliquot portion to a Nessler tube, add 10 cc. of a saturated hydrogen sulfide solution, and calculate the lead present from the amount added to a standard solution, which matches it in color. When preparing the standard solution add to each tube, before the addition of the hydrogen sulfide, the same quantity of reagents[12] as used in the analysis of the sample. If the tint of the unknown sample differs from that of the standard, ignite the precipitated calcium and lead sulfates below redness before digesting with the ammonium acetate solution.

Arsenic

Weigh 5 g. of the original acid into the generating flask of the apparatus used for the determination of arsenic by the Gutzeit[13] method and complete the determination in the usual way, omitting the addition of the potassium iodide solution.

Total Sulfur

Transfer an aliquot part of Solution A, containing about 10 g. of acid, to a 250-cc. beaker, dilute with water, add 10 cc. of dilute hydrochloric acid, oxidize with bromine water, boil off excess of bromine, and precipitate sulfates with barium chloride in the usual way.

Chlorine

Transfer an aliquot portion of Solution A, containing 2 to 5 g. of the acid, to a 150-cc. beaker, dilute to 100 cc., and add 5 cc. of concentrated nitric acid. Prepare a set of standard solutions containing from 0.5 to 5.0 cc. of a 0.1 *N* sodium chloride solution, and add to each 5 cc. of concentrated nitric acid and C. P. phosphoric acid equivalent to that in the sample taken for analysis. Add to each solution 2 cc. of a 1 per cent silver nitrate solution and calculate the chlorine in the unknown sample from the sodium chloride content of the standard solution which matches it in turbidity. It is important that the comparisons should be made before any appreciable darkening of the silver chloride occurs.

Fluorine

Weigh about 10 g. of the original acid into a casserole or evaporating dish, dilute somewhat with water, and add a thin paste of milk of lime until a permanent pink color is obtained with phenolphthalein. Evaporate to dryness on the water bath and ignite at 300° to 400° for about an hour, cool, weigh, and transfer to a stoppered bottle. Determine fluorine in 1 to 5 g. of the dried residue by the Wagner-Ross method.[14] This method was found to give low results when using the distilling flask represented in the original description of the method, but good results were obtained by a modification of the apparatus which will be described in a future paper.

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[6] J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis," 607.

[7] A. A. Blair, "The Chemical Analysis of Iron and Steel," 7th edition, 264.

[8] A. A. Blair, *Loc. cit.*, 265.

[9] J. E. Stead, *J. Soc. Chem. Ind.*, **8** (1889), 965.

[10] H. E. Walters, *Chem. News*, **84** (1901), 239; W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Surv., Bull.* **700**, 137.

[11] *J. Assoc. Official Agr. Chem.*, **4** (1920), 218.

[12] Ammonium acetate has little or no effect on the depth of color that develops in this test and its addition to the standard solutions may therefore be omitted if that used in the determination is known to be entirely lead-free.

[13] Assoc. Official Agr. Chem., "Methods of Analysis," 2nd edition, **1920**, 147.

[14] This Journal, **9** (1917), 1116.

Studies on the Nitrotoluenes[1]

VIII—Binary Systems of *m*-Nitrotoluene with Another Mononitrotoluene

By James M. Bell[2] and Joseph L. McEwen

University of North Carolina, Chapel Hill, North Carolina

THIS paper contains the data and the curves for the binary systems of *m*-nitrotoluene with *o*-nitrotoluene and with *p*-nitrotoluene. The data and curve for the binary system of *o*-nitrotoluene with *p*-nitrotoluene have already been given in the fifth paper of this series, by Bell, Cordon, Spry and White.[3]

The effect of other components on the freezing point of *m*-nitrotoluene has been studied by Jona,[4] with a range never over 6 per cent of the second component.

Menschutkin[5] has made a complete study of binary systems of *m*-nitrotoluene with a halide of antimony and found a compound (1 : 1) in two cases.

In a recent paper, Gibson, Duckman and Fairbairn[6] have given data for the system *m*- and *p*-. A brief comparison of their results with the present results is given below.

In the first stage in the nitration of toluene, all the three isomers, *o*-, *m*-, and *p*-, are formed. Such mixtures, of course, cannot be analyzed by direct methods. Consequently it becomes necessary to resort to some indirect means. This can easily be accomplished, for example, by preparing a chart of the freezing points of different mixtures of the compounds. Then, in order to analyze a sample mixture, it is necessary only to determine the freezing point of the sample in question, and refer directly to the chart. The value and use of such curves and charts are, therefore, quite obvious.

Purification of Compounds

Crude *p*-nitrotoluene was recrystallized several times from solutions in hot alcohol and benzene. It was filtered by suction and allowed to dry in a warm place. A constant melting point of 51.3° (cor.) accorded well with the earlier work.

m-Nitrotoluene was obtained in a pure form from the Eastman Kodak Company of Rochester, N. Y. The melting point of this compound was found to be constant at 15.53° (cor.).

o-Nitrotoluene was purified by partly freezing the liquid, decanting off the remaining liquid, allowing the crystals to melt, and again partly freezing.

By this process of fractional crystallization the impurities were left in the unfrozen liquid and were thus removed. This was done repeatedly until a constant melting point of −10.37° (cor.) was obtained for the metastable form. The melting point of the stable form was found to be −4.31° (cor.). These values agree very well with the work done before.

Experimental Procedure and Results

The weighed material whose melting point was to be determined was placed in an 8-in. test tube and provided with a looped-glass stirrer and a thermometer, graduated in 0.1°. This test tube was placed in a larger tube, in order to provide an air bath, and the whole was immersed in a bath which was approximately 10° below the freezing point of the mixture. Readings of the temperature were taken at regular

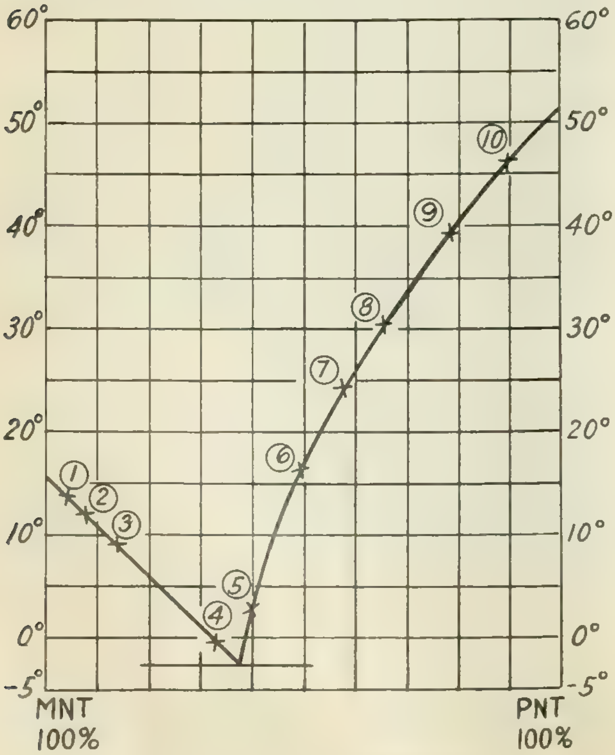

Fig. A Binary System of MNT-PNT

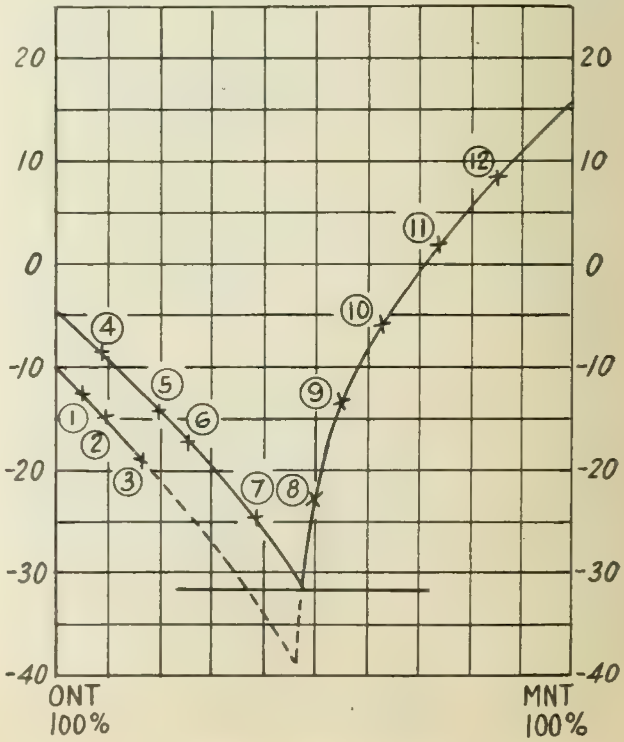

Fig B—Binary System of ONT-MNT

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[1] Received March 13, 1922.

[2] Professor of Physical Chemistry, University of North Carolina.

[3] This Journal, **13** (1921), 59.

[4] *Gazz. chim. ital.*, **39**, II (1909), 289.

[5] *J. Russ. Phys. Chem. Soc.*, **44** (1912), 1939, from *C. A.*, **7** (1913), 1176.

[6] *J. Chem. Soc.*, **121** (1922), 270.

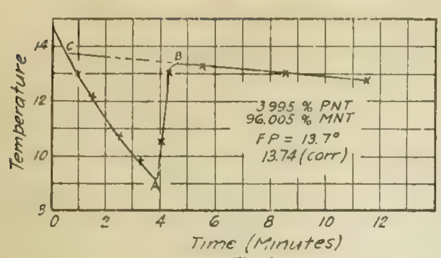

Fig. 1

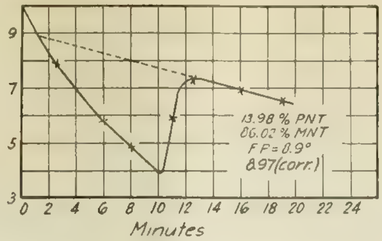

Fig. 3

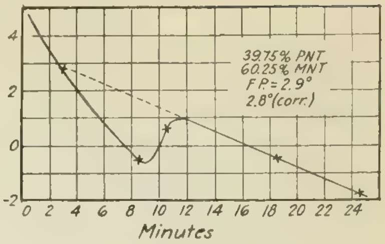

Fig. 5

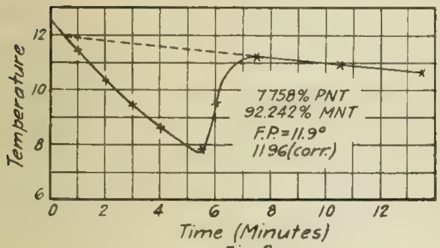

Fig. 2

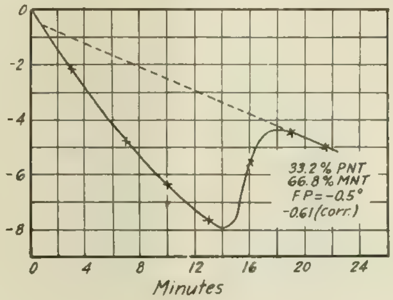

Fig. 4

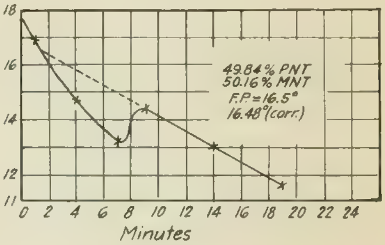

Fig. 6

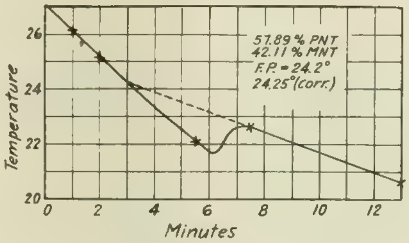

Fig. 7

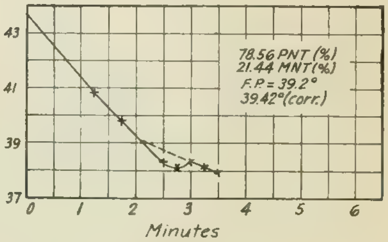

Fig. 9

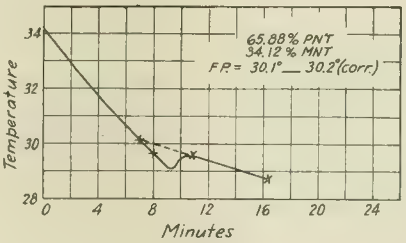

Fig. 8

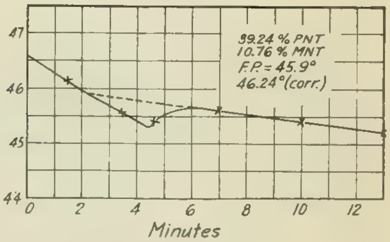

Fig. 10

intervals and the points were plotted. For temperatures above −15°, ice and salt were used, but for the lower temperatures, necessary in the binary system of *m*-nitrotoluene with *o*-nitrotoluene, solid carbon dioxide was used.

In the binary system of *m*-nitrotoluene with *p*-nitrotoluene, the eutectic temperature was found, by experiment, to be −2.8°, corresponding, from the chart, to about 37 per cent of *p*-nitrotoluene.

In the case of the binary system of *m*-nitrotoluene with *o*-nitrotoluene, the eutectic temperature was found by experiment to be −31.65°, corresponding, from the chart, to about 48 per cent of *m*-nitrotoluene.

Table I—Binary System: *m*-Nitrotoluene with *p*-Nitrotoluene

Per cent by Weight Meta	Per cent by Weight Para	Freezing Point ° C. (Cor.)
100.00	0.00	15.53
96.005	3.995	13.74
92.242	7.758	11.96
86.02	13.98	+8.97
66.8	33.2	−0.61
60.25	39.75	+2.8
50.16	49.84	16.48
42.11	57.89	24.25
34.12	65.88	30.2
21.44	78.56	39.42
10.76	89.24	46.24
0.00	100.00	51.3

Table II—Binary System: *m*-Nitrotoluene with *o*-Nitrotoluene

Per cent by Weight Meta	Per cent by Weight Ortho	Freezing Point ° C. (Cor.)
	Metastable Form	
0.00	100.00	−10.37
5.29	94.71	−12.66
9.52	90.48	−14.76
16.83	83.17	−19.3
	Stable Form	
8.86	91.14	−8.42
19.90	80.10	−14.11
25.74	74.26	−17.3
38.65	61.35	−24.57
50.09	49.91	−22.88
55.02	44.98	−13.41
63.65	36.35	− 6.1
73.89	26.11	+ 1.8
84.59	15.41	8.43
100.00	0.00	15.53

Explanation and Discussion

Supercooling was encountered regularly in these systems. Some investigators, in working upon the freezing points of binary mixtures, have taken the point at which crystals first appeared as the true freezing point. Others have chosen the maximum point of crystallization as the correct point. But, as has been shown in the third paper of this series, by Bell and Herty,[7] both of these methods are erroneous. The true freezing point of such a mixture can be obtained only by extrapolating that portion of the curve representing freezing liquid, back to the portion representing cooling liquid. This is the method that is here used in obtaining the true freezing points.

An examination of Fig. 1 will serve to make this more clear. A is the point at which crystallization began; B the maximum temperature of crystallization; and C the correct freezing point obtained by extrapolation. All of the points that have

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[7] This Journal, **11** (1919), 1124.

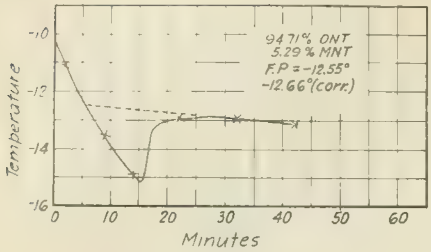

Fig. 1a

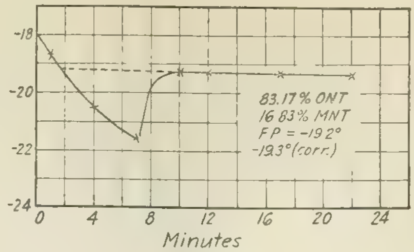

Fig. 3a

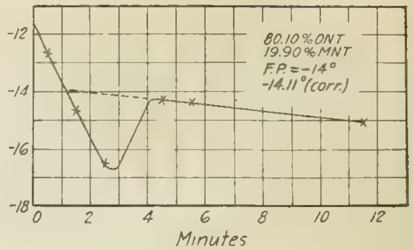

Fig. 5a

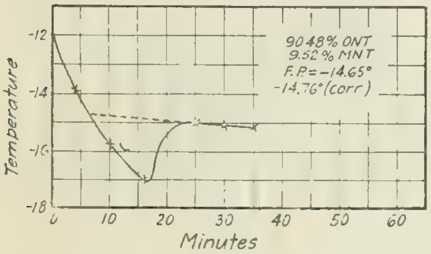

Fig. 2a

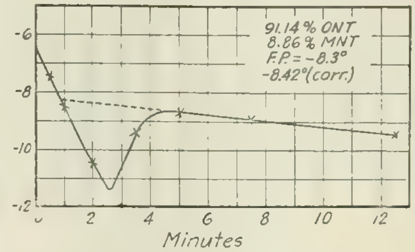

Fig. 4a

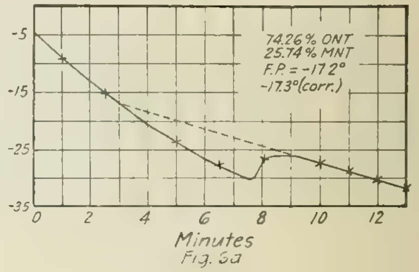

Fig. 6a

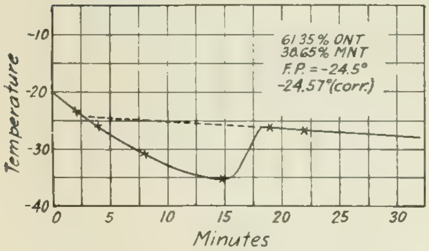

Fig. 7a

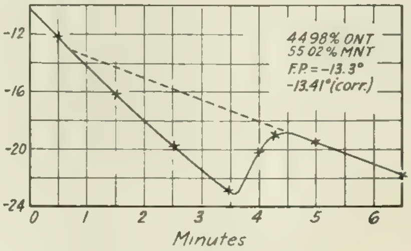

Fig. 9a

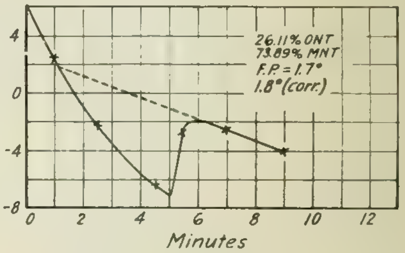

Fig. 11a

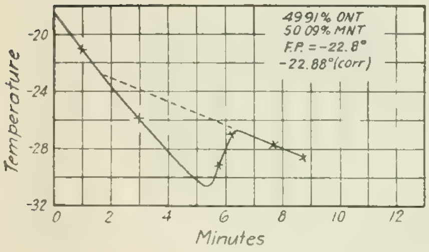

Fig. 8a

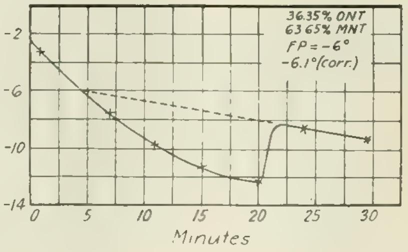

Fig. 10a

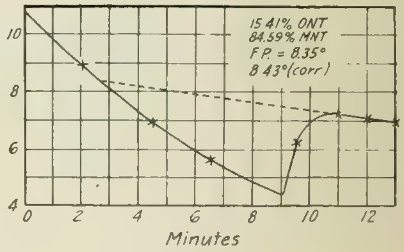

Fig. 12a

been used in plotting the curves for these binary mixtures were obtained in this way. For the sake of simplicity only a few of the readings taken have been indicated.

Fig. 1 corresponds to point No. 1, Fig. 2 to point No. 2, etc., of Fig. A. Similarly, Fig. 1*a* corresponds to point No. 1 of Fig. B, etc.

In the binary system of *m*-nitrotoluene with *p*-nitrotoluene there are very simple conditions, two curves meeting in a eutectic point. The diagram given by Gibson, Duckham and Fairbairn[6] indicates three curves, the third curve being very short and flat, and corresponding to the eutectic temperature which we have found. It seems probable that the freezing points as obtained by Gibson, Duckham and Fairbairn are too low, an error which would throw both the main curves too low. Furthermore, it is extremely unlikely that two components, as similar in structure as these, would form a binary compound.

In the binary system of *m*-nitrotoluene with *o*-nitrotoluene, it will be noticed that there are two curves on the *o*-nitrotoluene side. These represent the stable and metastable forms. The solid lines represent conditions which were attained. The broken lines have been sketched in and represent conditions which were not attained experimentally. The curve for the metastable form begins at −10.37° and descends roughly parallel to that of the stable form. It can be seen from the projected lines that if it were possible to reach the lower eutectic, it would probably be found to be about −39°, corresponding to about 46 per cent of *m*-nitrotoluene.

THIS JOURNAL has been given information concerning two highly recommended Italians who are desirous of representing American companies in Italy and acting as their agents to import into Italy chemicals, chemical apparatus, and supplies.

Purification of Gases from Methane[1]

By G. R. Fonda[2] and H. N. Van Aernem

RESEARCH LABORATORY, GENERAL ELECTRIC CO., SCHENECTADY, NEW YORK

In the following paper is described a method for the removal of methane from inert gases to be used in incandescent lamps. The method involves the decomposition of methane into carbon and hydrogen by passage through finely divided nickel at low temperature (about 500° C.), with subsequent removal of the hydrogen by passage through copper oxide at 500°. The passage of a gas containing 1.5 per cent methane, for example, through nickel at 500° reduces the content to 0.24 per cent, and a passage through a second series lowers it to 0.01 per cent.

The advantage in the use of nickel rather than copper oxide alone is that a lower temperature is possible. Under the same conditions of temperature and flow an equal volume of copper oxide gives less than one-eighth the decomposition caused by nickel. While a mixture of nickel and copper oxide will give equally good results, it has the disadvantage that the charge must be renewed upon exhaustion of the copper oxide. Oxidation of the exhausted mass leads to oxidation of the nickel at as low a temperature as 275° C. Nickel oxide in such a mixture is not catalytic and the mass is no more efficient than copper oxide alone.

It has been established by experiment that the constant for the reaction obtained by Mayer and Altmayer holds fairly closely for the reaction at the low partial pressure of 0.03 atmosphere.

CONTROL of the hydrocarbon content is one of the essential features in the preparation of gas for use in incandescent gas-filled lamps. Whether nitrogen or argon, it must be free from such substances as attack the tungsten filament or lead to discoloration of the lamp. Of the common impurities hydrogen may lead to destruction of the filament and blackening of the bulb through the formation of moisture from whatever oxides are present, and carbon monoxide and dioxide cause a less pronounced discoloration, and attack the filament slightly. All of these three gases are, however, readily removable.

Hydrocarbons are much more objectionable impurities. They decompose in contact with a glowing tungsten filament and the carbon liberated is absorbed by the tungsten as carbide, which in very small amounts renders the filament extremely brittle. To remove them from the gas is furthermore a difficult matter. In the usual procedure, which consists in passage of the gas over copper oxide, such a high temperature is required that early deterioration of the enclosing tube is likely to take place, as well as a sintering of the copper oxide, which makes purification still more difficult.

It was with the aim of facilitating the purification that some experiments were made with nickel as a catalyst for its decomposition, a reaction which it was thought might proceed readily at a lower temperature than is possible in its oxidation by copper oxide. Such a reaction was studied for methane at atmospheric pressure by Mayer and Altmayer.[3] They developed a thermodynamic equation for expressing the extent of the decomposition at various temperatures, based on determinations of the equilibrium constant in the equation

$$CH_4 = C + 2H_2.$$

This equilibrium bears on the present problem, for methane is formed when other members of the hydrocarbon series are heated and it is the most resistant to chemical attack. Its decomposition by nickel seemed to be particularly appropriate here because of the low partial pressure which methane would have as an impurity in a neutral gas. The reaction leads to an increase in volume, resulting in a shift in the equilibrium toward greater decomposition as the pressure of the methane is reduced. If the equation given by Mayer and Altmayer holds at these low partial pressures, it promises a ready purification by passage of the gas through nickel at a low temperature. The hydrogen liberated could be removed by copper oxide, likewise at low temperature.

EXPERIMENTAL

With the aim, therefore, of investigating this equation, an apparatus similar to that of Mayer and Altmayer was made up and nitrogen containing about 2 per cent methane was passed through the nickel catalyzer and the equilibrium in the outcoming gases determined.

Methane was made by the aluminium carbide and water reaction and diluted with nitrogen. On its way to the catalyst chamber it was further purified by passing over copper and copper oxide at 280° C. to remove traces of hydrogen, carbon monoxide, and oxygen, and then through soda lime, phosphorous pentoxide, and sulfuric acid.

The nickel catalyzer was obtained as a finely divided powder on asbestos feathers, soaked in nickel nitrate and heated in hydrogen. Three cc. were prepared in a quartz tube, and placed inside an alundum tube, heated electrically by two separate windings, one occupying the middle, and the other placed on the ends to compensate for cooling. The adjustment of a uniform temperature, as well as its maintenance, were secured by exploring with a small thermocouple. The whole was packed in alumina.

This catalytic chamber was followed by a copper oxide furnace at 850° C., in which the hydrogen liberated by the dissociation of methane over the nickel was burned to water. In addition the undissociated methane, stable at equilibrium, was completely oxidized to water and carbon dioxide.

The composition of the original mixture was found by passing through phosphorus pentoxide the gas which came from the copper oxide furnace, and weighing the water, which corresponded to the original content of methane. This proved to be 2.23 per cent.

The composition of the gas at equilibrium was determined from the carbon dioxide formed in the copper oxide furnace by passing the gas through 0.2 N barium hydroxide solution. The consumption of 0.2 N barium hydroxide, as given in the table, yields then the partial pressure of methane stable at equilibrium. The partial pressure of hydrogen was calculated from the amount of methane decomposed by the catalyst. As one molecule of methane yields two molecules of hydrogen the latter is equal to twice the difference between the original methane content and that stable at equilibrium.

Because of the fact that carbon was deposited in the nickel and might contaminate the catalyst, only short runs were made. In order to measure accurately the small amounts of gas involved the emerging gas was passed into a large buret, 4 cm. in diameter and 1.5 m. long, calibrated for volume, and filled with water. A manometer was attached to aid in maintaining the pressure at atmospheric as the water flowed out.

The thermodynamic equation of Mayer and Altmayer has the following form:

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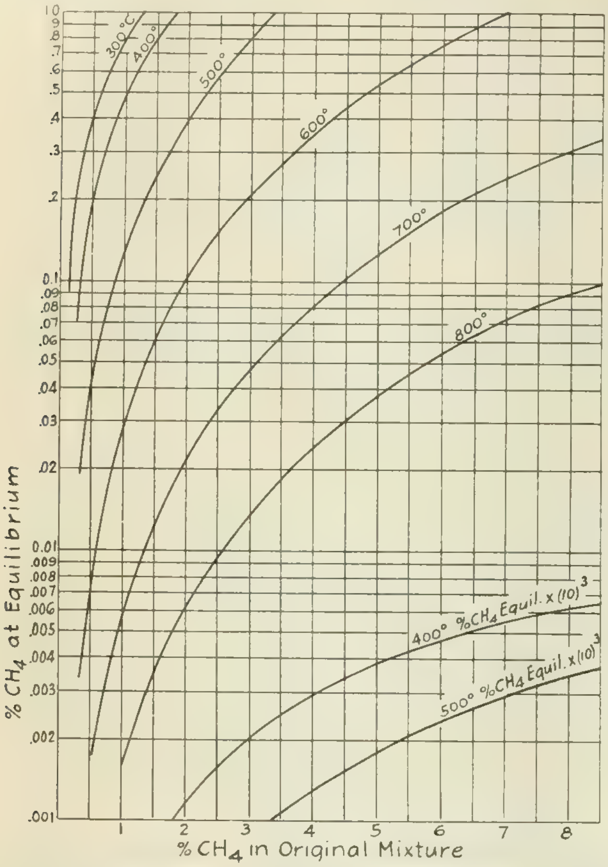
[1] Received February 9, 1922.

[2] Research Chemist, Research Laboratory, G. E. C.

[3] *Ber.*, **40** (1907), 2134.

$$\text{Const. } T = -18{,}507 + 5.9934T \ln T + 0.002936T^2 + RT \ln \frac{P_{CH_4}}{P_{H_2}},$$ based on the following values:

Heat of formation methane at 18°	= 20,500 cal.
Specific heat per mole hydrogen	= 6.5 + 0.0006T
Specific heat per mole methane	= 9.106 (20–208° C.)
Specific heat per atom carbon	= 2.0994 + 0.001736T



EQUILIBRIUM PRESSURES OF METHANE IN NITROGEN-ARGON MIXTURES

Results are given in the accompanying table.

DECOMPOSITION OF METHANE (2.23 PER CENT IN NITROGEN) BY PASSAGE OVER 3 CC. OF NICKEL-ASBESTOS

Temp. ° C.	Gas Liters	Flow Cc. Min.	0.2 N $Ba(OH)_2$ Cc	Partial Pressures at Equilibrium CH_4	H_2	CONSTANT
550	0.465	72.0	1.60	0.0075	0.0296	24.4
550	0.415	56.8	1.35	0.0071	0.0304	24.2
550	0.415	83.0	1.66	0.0087	0.0272	25.0
550	0.440	45.5	1.35	0.0066	0.0314	23.9
550	MEAN	..	..	0.0075	0.0296	24.4
440	0.355	51.2	2.19	0.0134	0.0178	23.0
440	0.380	50.3	2.20	0.0126	0.0194	22.6
440	0.405	58.2	2.24	0.0121	0.0204	22.3
440	0.460	68.0	2.15	0.0102	0.0242	21.2
440	0.385	56.2	2.24	0.0127	0.0192	22.6
440	0.400	63.5	2.16	0.0118	0.0210	22.1
440	MEAN	..	..	0.0125	0.0205	22.3

The values for the constant show very close agreement at any one temperature, well within the limits of error of the previously cited experiments at atmospheric pressure. There is, however, a consistent difference between the values for 550° C. and for 440° C. As the conditions were the same in both cases, and as the difference is in the opposite direction from what would be expected if it were due to failure to reach equilibrium at the lower temperature, there would seem to be some significance to be attached to it. In recent years the specific heat of hydrogen has been more accurately determined,[4] but the use of these values does not change the relationship. The change of the specific heat of methane with temperature is, however, still unknown and also the effect of low pressure on the specific heats. In spite of these uncertainties the error shown in the values of the constant at these two temperatures is only about double the error between the experiments at atmospheric pressure.

Mayer and Altmayer's value for the constant of 21.6 would seem therefore to be sufficiently close to 23.3, the mean found in these present experiments, to indicate that the equation as stated by them holds at least fairly closely for the reaction at the low partial pressure of 0.03 of an atmosphere.

Passage of this mixture of nitrogen with 2 per cent methane through copper oxide alone having the same volume as the nickel powder yielded less than one-eighth the extent of decomposition secured by the nickel under the same conditions of temperature and flow.

To demonstrate more particularly the advantage of the nickel catalyst in eliminating methane impurities from inert gases, the equation was used to calculate the decomposition for amounts less than 8 per cent methane, and at temperatures ranging up to 800° C. For the constant Mayer and Altmayer's value of 21.6 was taken. The results are given in the series of curves in the attached figure. They show, for instance, that for a gas containing as much as 1.5 per cent methane, one passage through nickel at 500° C. reduces its content to 0.24 per cent, and passage through a second similar series lowers it still further to 0.01 per cent. In each case the nickel furnace should be followed by one containing copper oxide, also at 500° C., to remove the hydrogen liberated.

Instead of using sequences of such furnaces, it was found that a mixture of nickel and copper oxide in the same furnace secured equally good results. The disadvantage of such an arrangement, however, lies in the necessity of renewing the charge on exhaustion of the copper oxide. Oxidation of the exhausted mass was found to lead to oxidation of the nickel as well as of the copper, even at as low a temperature as 275° C. Nickel powder was found to be oxidized, though at a rate less than one-ninth that of copper powder of the same fineness. In such a mixture, nickel oxide failed to exercise any catalytic function, and the mass was found to be no more efficient than copper oxide alone in the removal of methane.

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[4] W. Escher, *Ann. Physik.*, **42** (1913), 761.

Cleaning of Museum Exhibits

Bulletin 5, published by the Department of Scientific and Industrial Research, H. M. Stationery Office, London, is an interesting account of investigations conducted at the British Museum under the direction of Dr. A. Scott. It deals with the cleaning and restoration of such museum exhibits as prints and enamels, silver, lead, iron, and copper articles, and prehistoric paintings on rocks.

Brown spots on prints, the result of growth of mold fungi, are best removed by very dilute bleaching agents. Thymol and similar antiseptic agents have given promising results as mold preventatives, especially when aided by heat. Brown stains due to oils or varnishes cannot be removed by bleaching agents, but yield to pyridine, which does not affect the paper.

To remove the crust of copper oxides, carbonates, and oxychlorides from silver-copper alloys a warm dilute formic acid solution is a safe reagent which does not attack the silver or the alloy. Other agents for this purpose are a solution of ammonium sulfite and ammonia containing some cuprous sulfite, a solution of ammonia and ammonium formate, or zinc dust moistened with very dilute sulfuric acid.

Ammonium chloride, either alone or with stannous chloride and a little hydrochloric acid, is more satisfactory than ammonia for removing superficial deposits from objects of copper, bronze, or brass. An alkaline solution of Rochelle salt will also give good results.

The lichens on rock paintings from Northern Rhodesia could not be removed by mechanical means. They were softened and gelatinized by painting with dilute ammonia, and brushed off. The rock was then washed with distilled water and finally with absolute alcohol.

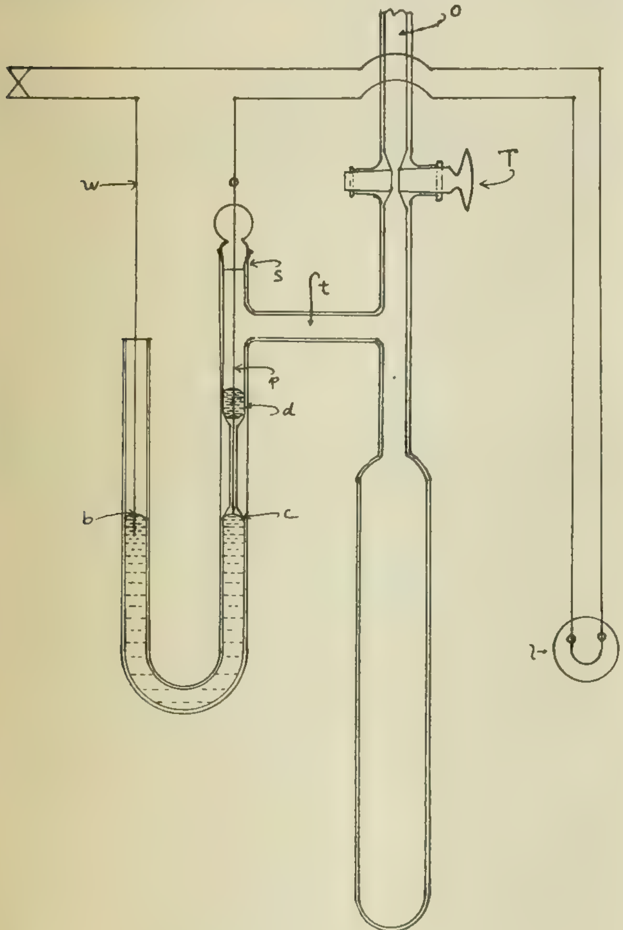
Thermo-Regulator[1,2]

By **E. B. Starkey** and **N. E. Gordon**[3]

University of Maryland, College Park, Maryland

THIS thermo-regulator was designed to meet the needs of the individual student in physical chemistry. It has an accuracy to 0.05° C., and does not require relay or battery. Furthermore, the point of contact is enveloped in an atmosphere of inert gas, and, hence, there is no oxidation at the point of contact.

The accompanying figure shows the model that was designed to meet the above requirements. The U-tube is filled with mercury until level with the bottom of the capillary tube *c*. The capillary tube which has a diameter of 0.50 mm. is then sealed by a drop of mercury, *d*, put in through *s*, enclosing a column of air in the capillary. This air after one or two contacts is deprived of its oxygen, leaving inert nitrogen. The rest of the thermo-regulator is easily filled with toluene through *o*. When the toluene has gone over through *t* and finished filling the U-tube, a ground-glass stopper is firmly placed in *s*. The filling is continued until the toluene passes up through the stopcock T. The thermo-regulator is now ready for use. It is placed in series with an electric light, *l*, from a 110-volt line. One contact is made at *b* and the other at *c*. The *b* contact may be made by means of ordinary copper wire, *w*, but the contact at *c* is made by means of a platinum wire, *p*, 0.355 mm. in diameter, passing through the ground-glass stopper and just reaching to the surface of the mercury at the bottom of the capillary tube.



The light *l* and thermo-regulator are placed in the bath, and the current is turned on, with the stopcock at T open. As the temperature rises the toluene expands up into the tube above the stopcock T. When the desired temperature has been obtained the stopcock T is closed, and any further expansion results in breaking the contact at *c*, when the light goes out. As soon as the bath begins to cool, contraction takes place and contact is again made at *c*, when the light is again thrown on. The inert gas acts as a condenser and scarcely any spark is noticeable, and since this slight spark takes place in an inert gas no corrosion at the point of contact results.

The commendable features which our thermo-regulator claims are:

1—The ease with which it can be made and filled.
2—The ease with which it can be regulated.
3—The doing away of relay and battery.
4—The protection of the point of make and break from all corrosion.

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[1] Received February 7, 1922.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[3] Professor of Chemistry.

Creative Thought

By **H. W. Jordan**

133 Stolp Ave., Syracuse, New York

"Creative thought has raised man from his pristine, subsavage ignorance and squalor to the degree of knowledge and comfort which he now possesses. On his capacity to continue and greatly extend this kind of thinking depends his chance of groping his way out of the plight in which the most highly civilized peoples of the world find themselves. Creative thought is the only hope of the future."

Prof. James H. Robinson, in "The Mind in the Making," a book recently issued by Harpers, sets forth the profound contrast between the dynamic, creative thought of the scientists and the static, frozen thought of the directors of mental life, especially those of government and education. We are oppressed by war and social chaos because the scientists' type of thinking has not been applied on any considerable scale to the solution of those world problems that spring from modern city industry operated in an eighteenth-century intellectual environment.

"It is an easily demonstrated scientific truth that in all ranks may be found evidence of unrealized capacity; and that we are living on a far lower scale of intelligent conduct and rational enjoyment than is necessary," says Professor Robinson. He makes it plain that if we would tap the limitless reservoirs of creative thought we must explore them by scientific research and by science applied to the social mass mind as we have applied it to the potential forces of nature.

Slavish bondage to such incongruous practices as assembly of our national congress thirteen months after its election, and inauguration of our President four months after his election, in an age when assemblywomen fly to Topeka, is proof that mental habits continue long after their purpose has ceased and their origin has been forgotten.

Among efforts to improve business and to place our modern chemical and engineering industries far ahead of normalcy, the most promising is creative thought applied to the mass human mind by scientific research.

"The Mind in the Making" is regarded by many chemists as the most illuminating recent scientific analysis of the social industrial situation.

Can We Afford to Make Potash in America?[1]

By R. Norris Shreve

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In the last few years we have devoted a great deal of time, effort, and money to the development of an American potash industry, and we have marshaled many facts in support of the establishment on a permanent basis of this industry so essential to the safeguarding of the productivity of our farm lands. Is it not now an opportune time to pause and ask ourselves the broad question—"Can we afford to make potash in America?" This question is an especially timely one in view of the position taken by the domestic potash industry that temporary tariff protection is necessary to carry the industry over its development stage and until it has worked up its by-products, and has cheapened the cost of production.

As a basis for this argument, reference is made to Table I, giving statistics and prices pertaining to the potash industry. No differentiation is made between potassium salts used in the chemical industry and in fertilizers. However, the fertilizers consume about 90 per cent of the country's total. The prices in this table refer to those that were paid chiefly by the fertilizer industry. The prices charged for potassium salts which are used chemically are based on these fertilizer prices, enhanced by the cost of purification or conversion, as the case may be.

Table I

Year	Tonnage of Actual Potash Imported Short Tons	Tonnage Manufactured in U. S. Short Tons	Tonnage Manufactured and Sold in U. S. Short Tons	Value of Domestic Sales per Ton K_2O	German Muriate Potash Net Syndicate Contract Price c.i.f. Atlantic Ports Basis 80 Per cent Dollars	Spot Ton Prices Muriate of Potash Basis 80 Per cent Dollars
1910	279,780	....	....	...	32.98	About 38
1911	274,446	....	....	...	35 75 32.34	About 38
1912	253,678	....	....	...	32.34	38.05–38.55
1913	270,720	....	....	...	32.34	38.55–38.65
1914	207,089	....	....	...	33.21	39.07–39.57
1915	48,867	1,090	1,090	314	...	39.57–356
1916	7,885	9,720	9,720	437	...	475–290
1917	8,100	32,573	32,573	429	...	450–325
1918	7,957	54,803	38,580	411	...	345–260
1919	39,619	32,474	45,728	231	...	260– 85
1920	224,792	48,077	41,444	180	32 00	300– 85
1921	73,887	9,000	?	...	32.00	85– 35

Farmers' cash price for muriate of potash, basis 80 per cent, bagged and tagged in ton lots, f. o. b. Atlantic ports, was $37.50 in the early part of 1914, and $39 in 1921. The Schmidtmann price for muriate of potash, basis 80 per cent, c. i. f. Atlantic ports, was $20.40; this was on contract to the large users in 1910.

The table indicates a total annual consumption in the years preceding the Great War of around 250,000 tons of actual potash, under the stimulus of a very active potash propaganda on the part of the German Potash Syndicate. An annual consumption of 200,000 to 225,000 tons of actual potash will probably satisfy all the country's pressing demands for some time to come.

We may interject here an explanation of what is understood by "actual potash" and by "a unit of potash." Actual potash refers to potassium oxide or K_2O. It was adopted as the only means of designating the value of the potassium salts, varying as they do all the way from 12 per cent actual potash or K_2O, in the form of kainite, to 60 per cent actual potash or K_2O, as in 95 per cent muriate of potash (potassium chloride). When sold to the fertilizer trade these salts are always based on a stated percentage of actual potash or K_2O. As a rule, for the fertilizer industry it is only the actual potash content that determines the usefulness of these potassium salts. However, certain salts are better for certain crops than others; for example, potassium sulfate works better on tobacco than potassium chloride because any chloride lowers the quality of this crop.

It has become customary to state the composition of fertilizer mixtures as containing so many units of ammonia, phosphoric acid (as P_2O_5), and potash (as K_2O). In each case a unit stands for 20 lbs. of the constituent, and equals 1 per cent on basis of a ton of 2000 lbs. Hence, a ton of 2:8:4 fertilizer contains 2 units or 40 lbs. of ammonia, 8 units or 160 lbs. of phosphoric acid (as P_2O_5), and 4 units or 80 lbs. of actual potash (as K_2O).

Proposed Tariff Legislation

The duty in the tariff bill, passed by the House of Representatives, imposed the following specific duties on crude potassium salts imported into the United States, said duties being based on the weights of actual potash in these salts.

Dating from Passage of Tariff Bill	Rate per Lb. of Actual Potash Cents	Rate per Ton of Actual Potash Dollars
First year	2.5	50
Second year	2.5	50
Third year	2	40
Fourth year	1.5	30
Fifth year	1	20
Thereafter	Free	Free

The average rate for the 5-yr. period is $38 per ton of actual potash. A unique feature of this proposed protection is that the industry feels that after five years it will have so developed its processes and by-products and so cheapened its manufacturing methods that it can compete on a free basis with the world.

All facts point to this decrease in cost. For example, one large company experienced the following cost ratio:

Assuming that during the first four months of 1919 their cost was 100
then during the first four months of 1920 their cost was 58.3
and during the first four months of 1921 their cost was 32.6

Furthermore the average cost per unit of potash (20 lbs. of actual potash or K_2O) for a number of operating plants was $4.24 in 1918–1919, while in 1920 this had been reduced to $2.04, with the sure prospect of reducing this figure to around $0.70 or lower, if the opportunity for operation and further development is given again.

By an inspection of Table I, it can be seen that the 1921 production was only 9000 tons of actual potash, for the reason that practically all of the domestic plants were shut down. Costs cannot be cheapened under these conditions.

The Debit Side of the Potash Situation

To answer our question "Can we afford to make potash in America?" let us draw up a balance sheet with debits and credits as an accountant does.

In the first place what have we on the debit side, or what is it going to cost us to establish this industry here? The almost unanimous opinion is that the cost will be measured by the tariff protection as given in the House tariff bill. As has already been said, this bill grants an average protection of $38 per ton of actual potash for five years. It is certain that this will not increase the present prices by the full $38, for the Germans can and undoubtedly will sell lower to get their share of the business. Assume that they cut their present prices $10 to $15 per ton of actual potash, we shall then get an increase of $25 per ton of actual potash. The increase will apply to both domestic and imported potash, and for an annual consumption of 200,000 tons of actual potash, there will be an annual charge of $5,000,000, which will go on for five years.

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[1] Received March 31, 1922. Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

The Credit Side

This is the only item on the debit side that the writer has been able to find. Turning now to the credit side, what have we to balance against this annual charge of $5,000,000? First, we shall save taxes by the amount of tariff paid. The best estimates are that under this tariff our domestic plants will produce annually 100,000 tons of actual potash, leaving 100,000 tons to be imported. The domestic plants did produce 54,000 tons of actual potash in 1918, and have a capacity to produce the 100,000 tons and will do so when economic conditions warrant. The tariff paid per annum on 100,000 tons at $38 per ton will equal $3,800,000; this is our first credit item. Without this, the country will have to pay this sum in taxes levied in some other way.

According to the latest statistics, the capital invested in potash plants in America was $28,696,143.[2] This value is a conservative one. If the American potash industry receives this temporary tariff protection, most of this capital will prove a good investment.

Our next credits are interest and capital write-off (or depreciation) on this investment. The interest at 6 per cent amounts to $1,700,000, and the capital write-off (or depreciation) at 5 per cent amounts to $1,400,000 annually. While we are considering the item of capital, attention may be called to the fact that some $30,000,000 invested in America can produce 100,000 tons of actual potash, while Germany has an investment of $380,000,000 to produce 1,100,000 tons of actual potash. This rate is slightly more than the American.

If the American potash industry is firmly established, it will give employment directly to about 3000 men and be the means of livelihood for some 12,000 men, women, and children. At an average of $20 per week, there will be paid to Americans over $3,000,000 annually in wages. In these days of unemployment, this feature is an important one, especially from an economic viewpoint.

Writing of prices of fertilizer constituents in the "Report on the Fertilizer Industry," the Federal Trade Commission states that the wholesale prices of nitrogen compounds and phosphates are due to natural conditions of supply and demand, while "the wholesale prices of potash salts, on the other hand, are governed by monopoly conditions."

Why do we pass laws to prevent monopoly within our own domain, and yet not even discourage a foreign monopoly? Furthermore, what treatment can we expect of this monopoly? We do not need to turn back many years to find an example of the actions of this "potash monopoly." In 1909 the Schmidtmann interests in Germany, on the occasion of a temporary break-up in the Potash Syndicate, made contracts with American consumers to sell them what amounted to 90 per cent of America's total requirements at a price reduction of from 25 to 38 per cent from what the "Potash Monopoly" had charged. These Schmidtmann contracts resulted in a saving to Americans of around $3,000,000 annually.

The "Potash Monopoly," however, persuaded its partner, the German government, to pass the potash law of May 25, 1910, which acted to invalidate the Schmidtmann contracts, and to force the Schmidtmann mines into the Syndicate. Such is the policy of the "Potash Monopoly!" When we did make a good buy, the German government invalidated it. We must remember this in considering the potash situation. By establishing our American potash industry, we shall prevent any such happening. Judging by the past the only way that Americans can eventually secure cheap potash is by domestic competition with the potash monopoly. We are temporarily getting German potash as cheaply as we did before the war, but we must not forget that depreciated currency will not always prevail, and that it is costing more to produce potash in Europe now than it did before the war. These enhanced costs will be noticeable when the foreign exchange rights itself.

Many by-products from our potash industry will be developed if this industry is established here, and they will eventually cheapen the production to a marked degree. We have heard of borax, salt, sodium carbonate, sodium sulfate, and the like from the potash brines of the West. We have also in mind alumina as well as potassium salts from potash minerals, and even building bricks and agricultural lime, as such by-products.

In certain industries, such as those manufacturing alcohol and cement, we find potash as a by-product from established operations. This phase of potash production offers great possibilities, as for example in the smelting of iron ores in blast furnaces, provided that the incentive is here to collect these otherwise wasted potassium compounds. One of the smaller potential sources of by-product potash is in the scouring of wool which could easily yield 10,000 tons of actual potash annually, besides other valuable products.

Another credit that we should list on the right side of our balance sheet is that the potash industry is essential to safeguard the food and clothing of the nation. It is not necessary to dwell on this very emphatically, as we all are of one opinion that it is wiser to have within our own boundaries all industries that are necessary to the very life of the people. We do not want our potash industry to be in the hands of the nation that stated, in the words of Dr. Wilhelm Ostwald, "America went into the war like a man with a rope around his neck, which is in the enemy's hands and is pretty tightly drawn."

Several other phases of this matter need only to be mentioned. The development of our own industries by a tariff is the American way of doing things. But when did an industry ever before ask for a tariff decreasing and finally disappearing after five years? Furthermore, the development of American raw materials is one of the fundamentals of our economic life, and in the case of the potash industry our raw materials are almost inexhaustible.

To summarize our annual debits and credits we have

Debits		Credits	
Charge due to imposition of tariff.......	$5,000,000	Tariff revenue.......	$3,800,000
		Write-off or depreciation on capital already invested.....	1,700,000
		Interest on capital already invested.....	1,400,000
		Wages..............	3,000,000
	$5,000,000		$9,900,000
		Gain......	$4,900,000

This $4,900,000 does not include the various intangible credits which cannot well be valued in dollars. But the only hope of permanently cheap potash in America is to establish the domestic industry on a competitive basis.

The Situation for the Farmer

One final point remains to be considered. We may grant that the economics of the situation are such that it is to the financial advantage of the entire country to establish the potash industry, but what of the farmer? What price must he pay?

Over 75 per cent of our entire tonnage of fertilizer is used in the southeastern states, where the principal fertilizer is the "2:8:2" mixture, or one containing 2 units or 2 per cent of actual potash. The amount used per acre of cotton, for instance, varies; while 1000 lbs. should be employed, the amount is generally 500 to 600 lbs. On the basis of 600 lbs. of fertilizer, containing 2 per cent of potash, we have an additional charge of 22.8 cents per acre of cotton, provided the entire additional cost due to the average duty of $38 per ton of actual potash or 38 cents per unit, is added to the price. It is quite likely that this will be only two-thirds of this amount, or around 15 cents per acre of cotton or per bale of cotton—a very small amount.

The real way for the farmer to get cheap potash is to buy his own fertilizer constituents and to do his own mixing. The Federal Trade Commission in their "Report on the Fertilizer

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[2] Hearings before Committee on Finance, U. S. Senate, December 30, 1921, 4698.

Industry" point out (page 227) that the cost of materials to the fertilizer companies is from 61 to 68 per cent of net sales. And again this same report (on page 234) states "Nearly every Agricultural Experiment Station in the United States, as well as the United States Department of Agriculture, advocates the purchase and home mixing of fertilizer materials." Recently, the Connecticut Agricultural College, referring to Connecticut, made the assertion that "the possible saving by home mixing to-day would amount to somewhat more than $1,000,000." Many states could effect a larger saving than Connecticut.

This home mixing is increasing from year to year, and the farmer must realize that his chance of making fair purchases of potash is much greater from a number of *competing* American potash producers, than it is from the "Potash Monopoly," whose methods have always encouraged the larger users by quantity discounts.

Can the College Do Anything for Industry?[1]

By Edward Ellery

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THE business of industry is profits. There is nothing bad about that. The business of the hospital is cures. The buinsess of the school is enlightenment. The business of the church is spirituality. The business of the home is happiness. Each of the great organizations in human life has its particular business. If it fails to secure its ends, it has no reason for existence. So when one states that the business of industry is profits, he is only emphasizing what industry will try to accomplish.

Industry has been of vast help to all the other organizations in human life, especially by the contribution of large sums of money for their maintenance. The colleges have in particular been the beneficiaries of this largess. Such contributions are made from profits. Every college officer recognizes what these gifts have made possible in the way of advancement of knowledge and increase of enlightenment, and he asks himself—what can the college do, more than it has done, in return? What contribution can it make to industry? What more can it do to promote coöperation?

Among other things, the college, always remembering that the business of industry is profits, can reduce the period of unproductiveness of the graduates when they enter industry. Time is a factor in profits. It takes time for a college graduate to adjust himself to the requirements of industry. That time represents a loss to industry and by so much retards the accomplishment of its business.

One cause of this unproductive period is the method of instruction in our educational system. From the time he enters it to the time he takes the master's degree, the student is "passing courses;" he is learning lessons from textbooks or lectures (the lectures in most instances are but spoken textbooks) under the disciplinary presence of an older person or the disciplinary influence of a grade or degree, and on demand he reproduces what he has learned. The method is beneficial for a certain limited period. The compulsion to learn a definite number of facts, to do a definite thing in a definitely prescribed way is good for a lad up to, and even including a portion of, his college years. Prolonged beyond that point of usefulness, it becomes fatal to real mentality. It makes the mental mechanic, but not the intelligent master of ideas.

The college can and should teach the boy something else than how to learn a lesson or how to do a piece of work from detailed directions. It must so teach if it is to make a large return to industry. We will illustrate from the teaching of chemistry, of course. Can a textbook in General Chemistry be taught without teaching a textbook? Can we have a classroom and no classroom machinery? Can we have a schedule of appointments that take a student's intelligence from one problem to another while requiring him to move his body from one spot to another? Of course we can. What are we after? In general, four things —acquisition, recognition, application, and description of facts.

Shall the assignment be pages 1 to 10 in the textbook? Not at all. It shall be Boyle's and Charles' Laws. Shall the requirement be to commit those laws to memory together with the formula for their use in problems? Not at all. Require the student to learn the facts and give him twenty-five or fifty or a hundred problems to solve. Require him to make his own equations, to apply the quantities given in accordance with the facts. Then he will know the law and the formula.

Shall the laboratory assignment be Experiment 47? Not at all. The assignment is ether. The student should be required to discuss with his instructor what he proposes to do, how he proposes to do it, how he will know when he has done what he proposed to do, and finally to present for inspection and explanation not only a finished product but the residues of the reaction. That's the way to get facts, to recognize facts, to express facts, and to use facts.

The final requirement of a college course in chemistry should be the handling of an original problem. Without that kind of training a young chemist is bound to be an "unprofitable servant" in industry for some time after his graduation. With it, the period of unprofitableness can be materially reduced. To accomplish the result certain conditions are essential.

1—*Small instructional groups.* It is not the total number in college that affects the product. It is the size of the instructional group. Ten or a dozen at a time is about the maximum a good chemistry teacher can handle.

2—*Superior students separated from inferior students.* The two cannot be taught together. The combination harms the superior and does not benefit the inferior.

3—*The strongest and most experienced teachers over freshmen and seniors, the inexperienced or those with limited experience over sophomores and juniors.* The first year of college life is relatively the most important of the four and requires the finest and surest pedagogy. The final steps in the training likewise require the careful, direct supervision of instructors of long and successful experience. Neither the first nor the last year is a proper time for the pedagogical experiments of untried teachers.

4—*A limitation of the number of students and of hours the good teachers teach.* Fine pedagogy, as in every other relation of life where minds and spirits of human beings are in contact, takes "virture" out of a man. One must be given time to re-accumulate the power.

I think these are sensible suggestions. I would like to see colleges rich enough and strong enough to put them into practice. Industries can well afford to help colleges keep instructional groups small enough to be individualized, segregate superior students, and assign the best teachers to the first and fourth year men. Colleges will thus be able not only to produce better trained men, but to reduce by a considerable amount the length of the unprofitable period of the new man in a plant. This is a way in which the college can help industry.

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[1] Received April 27, 1922.

First Report of the Committee on Contact Catalysis

By **Wilder D. Bancroft**

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(Continued)

CORROSION

The poisoning of chemical reactions which take place rapidly in the absence of a catalytic agent is a phenomenon familiar to the chemist though not usually classified under that head. Aluminium and nickel should corrode readily in the air; but do not, owing to the formation of a film of oxide or hydroxide which protects the underlying metal. So long as iron is coated with a coherent film of ferro-ferric oxide, the amount of rusting is negligible. Parkerized or phosphatized iron is protected chiefly by an oil film and is thus analogous to the platinum black which is not a catalytic agent when covered with a film of grease. Lead and lead peroxide in sulfuric acid constitute the lead storage battery; but the peroxide plate is not a short-circuited cell because the peroxide coats the lead grid and keeps it from coming in contact with the acid. Curry[92] showed that copper-tin bronzes containing 40 to 65 per cent copper corroded but slightly when made anodes in sodium nitrate or sulfate solutions. Alloys richer in copper or richer in tin corroded badly under identical conditions. The resistance to electrolytic corrosion is due to the formation of a coherent film of stannic oxide. It is not too much to say that in most cases the corrosion problem is a film problem.

If we were to put calcium carbonate in dilute sulfuric acid and if the resulting calcium sulfate were to form a coherent film over the surface of the calcium carbonate, the reaction would come to an end as soon as the surface of the calcium carbonate was coated over completely. The apparent equilibrium would be more or less independent of the concentration of the acid. For a given size of calcium carbonate particles, apparent equilibrium would be reached when a definite amount of calcium sulfate had been reached. This is self-evident in a case of this sort; but the matter is not always quite so obvious. A certain war gas, which we will call A, gives a solid hydrolysis product. The same amounts of A were treated with 250 cc. of water and with 1000 cc. of water. When apparent equilibrium was reached, the acid was four times as concentrated in the first case as in the second. Experiments were then made with dilute hydrochloric acid solutions instead of with water and it was found that the presence of hydrochloric acid in moderate amounts had practically no effect on the amount of hydrolysis. The hydrolysis took place in every case until the ratio of hydrolysis product to undecomposed substance was a constant. Of course it should have been shown that this ratio varied with varying crystal size; but there were a good many loose ends after the war and this was one.

BENEFICIAL POISONING

While the poisoning of a catalytic agent is usually a thing to be avoided, Rosenmund and Zetzsche[93] have made use of what they call partial poisoning in order to increase the yield of any desired product. If an acid chloride, benzoyl chloride for instance, is dissolved in pure benzene and is then subjected to reduction by means of hydrogen and colloidal palladium, practically no benzaldehyde is formed. The authors consider that the benzene poisons the palladium. If the experiment is tried with ordinary benzene, a good yield of benzaldehyde is obtained.[94] This seemed to prove that some impurity in the benzene counteracted the poisoning. Instead of searching for the particular impurity in the benzene which had this effect, the authors have studied the effect of adding known amounts of definite substances to the pure benzene or other aromatic hydrocarbon. With 2 g. of benzoyl chloride in 10 cc. of xylene and using 0.7 g. palladium at 150°, addition of 1 mg. of thioquinanthrene brought the yield up to 78 per cent, while addition of sulfurized quinoline (impure thioquinanthrene) brought the yield up to nearly 90 per cent. Addition of 0.1 mg. distilled quinoline[95] reduced the yield practically to zero because the reduction went further—to benzyl alcohol. Addition of xanthone accelerates the reaction between benzoyl chloride and benzyl alcohol forming benzyl benzoate. In toluene as solvent instead of xylene, benzyl benzoate is the chief product because the toluene checks the reaction between benzyl benzoate and hydrogen which gives rise to benzoic acid and toluene.

It has also been found that addition of quinoline to benzyl alcohol dissolved in cymene increases the yield of benzaldehyde when copper is added and air is passed through the solution. A further addition of nitrobenzene increases the yield still more. In the absence of quinoline, copper, nickel, silver, magnesium, etc., behave about alike. Addition of quinoline makes copper, nickel, and silver much more effective than the others but in different ways, the copper increasing the oxidation to alcohol, while silver and nickel increase the formation of benzyl ether and of resins.

A case of what might be called protective poisoning has been studied by Palmer.[96] At temperatures below 300° pulverulent copper decomposes ethyl alcohol into acetaldehyde and hydrogen, with no formation of secondary products; but if a mixture of acetaldehyde and hydrogen is passed over the copper catalyst between 250° and 300°, much of the aldehyde is decomposed by secondary action. The author accounts for this apparent discrepancy by assuming that alcohol is adsorbed selectively by copper from a mixture of alcohol and aldehyde vapors, so that the surface of the copper during dehydrogenation is covered by a layer of alcohol molecules, these latter preventing the adsorption and consequent destruction of the aldehyde. Palmer believes that the dehydrogenation of alcohol involves three stages:

1—Adsorption of alcohol molecules over the surface of the catalyst.
2—Activation of certain alcohol molecules by absorption of energy.
3—Evaporation of acetaldehyde and hydrogen away from the adsorption surface into the alcohol stream flowing past the catalyst.

POSSIBLE SUBOXIDE OF ALUMINA

During the war kaolin was used as a catalytic agent to convert alcohol into ethylene as the first stage in the manufacture of mustard gas. In the course of time this kaolin became black and inactive. This was believed to be due to the precipitation of carbonaceous matter from the alcohol, a belief which seemed the more probable because the kaolin could be regenerated by heating with air. On the other hand, Ashby[97] reports that when alumina is made red-hot and quenched in absolute alcohol, it changes from white to black. Ashby says that this cannot be due to carbon from the alcohol because the same change occurs when heated alumina is quenched in strong ammonia. He suspects that the black color is due to a new oxide of alumina. This does not seem very probable; but the point should be cleared up definitely unless that has already been done.

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[92] *J. Phys. Chem.*, **10** (1906), 474.

[93] *Ber.*, **54B** (1921), 435, 638, 1092.

[94] Rosenmund, *Ibid.*, **51** (1918), 585.

[95] It is interesting to note that quinoline catalyzes the change from vitreous to metallic selenium, the action being more marked in sunlight than in the dark. Saunders, *J. Phys. Chem.*, **4** (1900), 469.

[96] *Proc. Roy. Soc. London*, **98A** (1920), 13.

[97] *Ibid.*, **7** (1855), 322.

STRUCTURE

Taylor[98] calls attention to the fact that a given solid catalytic agent can be so activated by suitable treatment that the apparent reaction temperature may be changed several hundred degrees.

> If hydrogen be passed over the copper oxide wire of commerce, rapid reduction begins in the neighborhood of 300°. If the copper so formed be oxidized at a somewhat lower temperature it will be found that subsequent rapid reduction will occur at a lower temperature than in the first reduction. This process of oxidation can be repeated to such a degree that the wire becomes sufficiently reactive to be reduced or oxidized at 100°; and examination of the wire shows that it is in a similar physical condition to that of the activated platinum used in the ammonia oxidation. Such copper oxide, moreover, will catalyze rapidly the combination of hydrogen and oxygen at 100°, whereas charcoal will be inert. We see therefore that in increasing the chemical reactivity of the contact agent we have increased its catalytic activity.

There seem to be at least four possible hypotheses in regard to the effect which a change in the structure of a catalytic agent has on the apparent reaction temperature.

1—The effect may be chiefly a question of total surface. Increasing the surface increases the adsorption per unit mass of the catalytic agent but not necessarily the adsorption per unit surface. With increasing surface there will be more reaction per unit mass in unit time, and consequently a reaction might be detected at a lower temperature than would otherwise be the case. It does not seem very probable that the increase in surface on activation is enough to account for the observed lowering of the apparent reaction temperature; but this is a question for quantitative measurements.

2—With increased surface and consequently reaction per unit mass of catalytic agent there will be increased evolution of heat per unit time. Unless suitable cooling is supplied, the temperature will rise. Since a porous catalytic agent is not a first-class conductor of heat and since the contact reactions are mostly exothermal, it is certain that the temperature at the contact surface is higher than the apparent temperature of the catalytic agent. It is a matter of quantitative measurements to determine whether the lowering of the apparent reaction temperature is real or illusory.

3—Changing the form of the surface may change the surface in such a way that the adsorption per unit surface is increased. This may very well be. While Langmuir claims that the adsorption layer is only one or two molecules thick on a plane surface, he is willing to admit that this may not hold true for a porous mass.

4—The change in the surface may be such that the reaction products pass off more rapidly and therefore do not slow down the reaction. If there were pockets, for instance, in the catalytic agent, the reaction would be removed only by diffusion. With an open structure, they would be swept out by the incoming gas stream and this might easily have a very marked effect on the reaction velocity.

We are not in a position to tell to what extent any or all of these four hypotheses will account for the facts. It may be that other supplementary hypotheses are necessary. We do not know whether the physical disintegration of the catalytic agent is due to the formation and decomposition of definite or indefinite chemical compounds or whether it is chiefly the result of a heat effect.

The question is complicated by some recent experiments by Kramer and Reid[99] on thoria. "When thorium nitrate is heated suddenly to a high temperature by being dropped into a red-hot crucible a very light, porous thoria is obtained, 7 g. of it occupying 200 cc. of space. On account of its enormous surface we expected this to be a wonderfully active form but found it inactive." There seem to be two possible explanations for this phenomenon. The bulky thoria may not be clean, and the structure of the surface may be important. The first possibility can easily be tested experimentally; but the second is more difficult. It is easy to imagine conditions under which a V-shaped surface might produce more effective activation than an equal area of a plane surface; but we have no satisfactory proof of this as yet. Briggs[100] considers that a vitreous surface always has a low adsorbing power.

INTERMEDIATE STAGES

It has been pointed out that, irrespective of any theory of contact catalysis, we ought to determine the intermediate stages in any given case and with special reference to the behavior of selective catalysts.[101] It is probable that the study of organic reactions is the most promising field. The reactions can take place in more different ways than with inorganic reactions and the intermediate compounds are easier to isolate and identify. The apparent theoretical simplicity of the catalysis of oxyhydrogen gas or of the synthesis of ammonia is deceptive. We know the initial and final states only. It is not going to be easy to determine the intermediate stages in the organic reactions and it will probably require the active coöperation of the organic chemist and the physical chemist; but it can be done. A few illustrations of what should be done may be desirable.

We know that ethyl alcohol can be decomposed into acetaldehyde and hydrogen or into ethylene and water; but that is as far as people have gone hitherto. With pulverulent nickel as catalyst, the reaction is almost completely

$$CH_3CH_2OH = CH_3CHO + H_2.$$

We do not know whether the hydrogen comes off in one stage or in two, though it is probable that it comes off in two stages. If so, is the first stage CH_3CH_2O or CH_3CHOH? With pulverulent alumina the reaction is almost completely

$$CH_3CH_2OH = CH_2:CH_2 + H_2O.$$

Does water split off as such or do we get a preliminary splitting-off of hydrogen or hydroxyl? It seems improbable that water can split off as such because then it would be difficult to account for the intermediate formation of ether. If the first stage is a splitting-off of hydrogen, it probably is not the same hydrogen which comes off first with nickel because then we should expect the reaction to go the same way in the two cases. If the first stage is a splitting-off of hydroxyl, does the other hydrogen come from the adjacent carbon atom, giving ethylene direct or does it come from the same carbon atom, forming a substituted methylene, CH_3CH, which then rearranges to ethylene?

Sabatier[102] and his co-workers have studied the action of various agents on esters and they find quite different reaction products in the different cases. With nickel the chief reaction is said to be as follows:

$$\begin{gathered} CH_3CO_2CH_2CH_3 = CH_3CH_2CH_3 + CO_2 \\ CH_3CO_2CH_3 = CH_3CH_3 + CO_2 \\ HCO_2CH_3(?) = CH_4 + CO_2 \end{gathered}$$

With thoria the decomposition is quite different:

$$\begin{aligned} 2CH_3CO_2C_2H_5 &= CH_3COCH_3 + CO_2 + (C_2H_5)_2O \\ &= CH_3COCH_3 + CO_2 + C_2H_5OH + C_2H_4 \\ 2CH_3CO_2CH_3 &= CH_3COCH_3 + CO_2 + (CH_3)_2O \\ 2HCO_2CH_3 &= HCHO + CO_2 + (CH_3)_2O \end{aligned}$$

With titania we have a third set of products:

$$\begin{aligned} 2CH_3CO_2C_2H_5 &= 2CH_3CO_2H + 2C_2H_4 \\ 2CH_3CO_2CH_3 &= 2CH_3COH + C_2H_4 \\ HCO_2CH_3 &= HCO_2H + CH_2 \\ &= CO + CH_3OH \end{aligned}$$

The decompositions are apparently regular and characteristic with each catalytic agent and the molecules must break or slip at different points in the different cases; but we certainly ought to know what the hypothetical intermediate stages are. Take the case of methyl acetate with nickel, for instance. One assumption might be that we have a methylene dissociation:

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[98] *Trans. Am. Electrochem. Soc.*, **36** (1919), 154.

[99] *J. Am. Chem. Soc.*, **43** (1921), 882.

[100] *Proc. Roy. Soc. London*, **100A** (1921), 97.

[101] Bancroft, *Trans. Am. Electrochem. Soc.*, **37** (1920), 51; "Applied Colloid Chemistry," **1921**, 45.

[102] Senderens, *Bull. soc. chim.*, **5**, [4] (1907), 482: Sabatier and Mailhe, *Compt. rend.*, **152** (1911), 669.

$$CH_3CO_2CH_3 = CH_3CO_2H + CH_2 = CH_3CH_3 + CO_2$$

A second assumption is that methyl splits off:

$$CH_3CO_2CH_3 = CH_3CO_2 + CH_3 = CH_3CH_3 + CO_2$$

A third assumption might be a splitting-off of both methyl groups:

$$CH_3CO_2CH_3 = 2CH_3 + CO_2 = CH_3CH_3 + CO_2$$

Is any of these what happens and how are we going to prove it? This should tie in with the other facts: that in aqueous solution acetate ion goes to ethane and carbon dioxide when set free at the anode,

$$2CH_3CO_2 = CH_3CH_3 + CO_2;$$

that iodine and silver acetate give a 50 per cent yield of methyl acetate[103] and silver iodide

$$2CH_3CO_2Ag + I_2 = 2AgI + CH_3CO_2CH_3 + CO_2;$$

and that dry lead tetracetate decomposes quantitatively at about 140° into lead acetate, methyl acetate, and carbon dioxide

$$Pb(CH_3CO_2)_4 = Pb(CH_3CO_2)_2 + CH_3CO_2CH_3 + CO_2.$$

The question also comes up as to the intermediate stages when the esters are chlorinated more or less completely. The fact that alumina splits superpalite to carbon tetrachloride and carbon dioxide, while ferric oxide splits it to phosgene suggests that there may be a reversal in the nature of the decomposition with increasing substitution by chlorine. It also makes one wish to know what ferric oxide would do to methyl and ethyl acetate.

In at least two cases it should be relatively simple to determine the reacting radicals. If a mixture of ethyl acetate and hydrogen is passed over pulverulent nickel, it is probable that some or all of the initial products will be reduced before they have time to react in the normal way. A study of the reaction products will therefore throw light on the probable mechanism of the reaction which occurs in the absence of hydrogen. If the chief products were ethane and ethyl formate, for instance, we should conclude that the original break had been into CH_3 and $CO_2C_2H_5$. If the chief products were acetic acid and ethane, we should be justified in concluding that these were reduction products of CH_3CO_2 and C_2H_5. If the reaction products were chiefly methane, ethane, and either carbon dioxide or some reduction product of it, we should undoubtedly assume that ethyl acetate splits simultaneously into CH_3, CO_2, and C_2H_5.

If ethyl ether is passed over pulverulent nickel, the dissociation will probably be either to $C_2H_5O + C_2H_5$ or to $C_2H_5OC_2H_4$. In the first case the final products will be ethylene and water, $2C_2H_4 + H_2O$, just as with alumina as catalytic agent, because alumina must decompose ether in this way. In the second case the final products are likely to be acetaldehyde, ethylene, and water, $CH_3CHO + C_2H_4 + H_2$, though the acetaldehyde may of course break down more or less and the ethylene may combine with the hydrogen to form ethane.

Work along these lines has been started by two members of the committee, by Professor Adkins at the University of Wisconsin and by Professor Chambers at Brown University. Preliminary results by Mr. Simon at Brown University indicate that at temperatures above 300° nickel decomposes ethyl ether primarily into acetaldehyde, ethylene, and hydrogen. At 355° ethylene is decomposed by nickel[104] into methane, ethane, hydrogen, and carbon. There is undoubtedly some hydrogenation of some of the reaction products.

Preliminary experiments at the University of Wisconsin on the action of nickel on ethyl acetate do not confirm the statements of the French workers. Instead of propane being the chief product, Professor Adkins has been unable to find any propane while working over a range of temperature from 250° to 400°. It is possible that this discrepancy may be due to some unrecognized differences in the experimental conditions; but this is an admirable illustration of the importance of verifying all the data and of getting the experiments in such a form that they can be duplicated by anybody. The importance of this is shown in some other results obtained by Professor Adkins. With ethyl acetate and alumina at 455° there are obtained for the first few minutes two volumes of ethylene to one of carbon dioxide, indicating that the reaction is taking place according to the equation

$$2CH_3CO_2C_2H_5 = CH_3COCH_3 + 2C_2H_4 + CO_2 + H_2O$$

which is what it should do. On longer running, this reaction becomes less important until, finally, only about one-third of the decomposition proceeds according to this equation, the remaining two-thirds being represented by the equation

$$CH_3CO_2C_2H_5 = CH_3CO_2H + C_2H_4.$$

With titania prepared by solution of titanium dioxide in concentrated sulfuric acid and precipitation with ammonia, or with titania bought from the Will Corporation, one-third of the decomposition was to acetone and two-thirds to acetic acid, just as with alumina which had been used for quite a while. When titania was prepared by precipitating blue titanous hydroxide from a solution of titanous chloride and then allowing this to oxidize to white titanic hydroxide while suspended in the solution, this catalyst caused two-thirds of the decomposition to be to acetone and one-third to acetic acid. Facts like these must be recognized in any theory which may be developed. Judging from the evolution of carbon dioxide, thoria converts ethyl and propyl acetates quantitatively into acetone according to the equations:

$$2CH_3CO_2C_2H_5 = CH_3COCH_3 + CO_2 + C_2H_5OH + C_2H_4$$
$$2CH_3CO_2C_3H_7 = CH_3COCH_3 + CO_2 + C_3H_7OH + C_3H_7$$

OXIDATION CATALYSTS

At the University of California Professor Bray is studying the catalytic oxidation[105] of carbon monoxide by air in presence of various oxides, such as those of cobalt, manganese, copper, silver, etc. He reports informally that:

> An oxygen carrier catalyst at the temperature at which it is operative should be able to oxidize the reducing agent used, carbon monoxide for instance, and should be restored to its original condition by the oxidizing agent, in this case the oxygen of the air. The actual catalysis involves a dynamic equilibrium in which two such processes take place simultaneously. The following experimental results seem to support the chemical theory of catalysis and particularly the idea of dynamic equilibrium. When a catalyst is operating at a temperature somewhat below that required for 100 per cent efficiency, a "steady state" is soon reached, under constant experimental conditions, in which the catalyst is operating at a definite efficiency. For example, it may operate at 60 per cent efficiency at a temperature 20° below that at which it operates at 95 per cent efficiency.
>
> These catalysts are highly adsorbent, porous materials, and it is not surprising that the catalyst is poisoned when easily adsorbable substances are present. When such a substance is inert and sufficiently volatile, the activity of the catalyst may be restored by an increase of temperature; water is a case in point. A catalyst which is active at room temperature or lower gradually becomes inactive and remains so when a moderate concentration of water vapor is present; but it operates again in a satisfactory manner under the same conditions if the temperature is raised to 70° to 90°. At room temperature enough water is adsorbed to form a capillary film in the pores of the catalyst granules, and it is evident that the poisoning effect in this case is due to the covering action of the film. Tests at a series of temperatures in the presence of a definite concentration of water vapor give a typical efficiency-temperature curve. With a lower concentration of water vapor a similar curve was obtained at somewhat lower temperatures. Preliminary results indicate

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[103] Simonini, *Monatsh.*, **13** (1892), 320.

[104] Rideal and Taylor, "Catalysis in Theory and Practice," **1920**, 220.

[105] This is a continuation of the work described by Lamb, Bray and Frazer, THIS JOURNAL, **12** (1920), 217.

that a rather inactive catalyst (for instance manganese dioxide, which does not operate at high efficiency with dry gas until a temperature of about 100° is reached) is also poisoned by water vapor and gives a similar efficiency-temperature curve at still higher temperatures.

For over two years it has seemed probable that carbon dioxide, the product of the reaction, might have a poisoning effect similar to that of water vapor but of course at lower temperatures. In fact it seemed probable that the desorption, or rate of removal, of the carbon dioxide might be the limiting factor in determining the lowest temperature at which an active catalyst would operate. The experimental work to decide this question is still in progress and, though incomplete, it seems probable that in many cases sufficient carbon dioxide is adsorbed to account for the decrease in activity of the catalyst at low temperatures.

One of the most active catalysts is a mixture of 60 per cent MnO_2 and 40 per cent CuO. It can be prepared by mixing the separate moist hydrated oxides before filtration and dehydration. It operates at a temperature as low as 0°, while the separate one-component catalysts prepared from its constituents are active only at much higher temperatures (*e. g.*, at about 100° from manganese dioxide). One of the most important problems is to account for the extraordinary increase in activity of the mixed catalyst compared with that of its components. It has been proved that the mixed catalyst is a much poorer adsorbent for carbon dioxide than is its principal constituent, manganese dioxide; but while this is very important it would not be safe to generalize on the basis of only one result.

(*To be concluded*)

The Elimination of Industrial Organic Odors[1]

By Yandell Henderson and Howard W. Haggard

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A method has been developed for the elimination of industrial organic odors by admixture of the gaseous emanation with very small quantities of chlorine gas. Since the total amount of odoriferous substance involved, even when a strong and exceedingly offensive odor is distributed over many square miles of territory, is very small in absolute amount, it is necessary to use only a correspondingly small amount of the deodorant agent. For the best results, the amount of chlorine must be adjusted with considerable quantitative accuracy. This process has been patented by the authors (1,410,249, March 21, 1922).

The use of chlorine has the advantage that it is already in use for the control of city water supplies, and apparatus for the control and precise adjustment of the flow of the gas is manufactured and already widely used. It can be readily adapted to the chlorination of air.

This method makes possible a great economy in the disposal of the garbage of a large city. All that is necessary is a simple drying plant in each division of the municipal area, rendered inoffensive by the chlorination of its effluent vapor. The dried material may then be collected in a central plant for extraction of grease or other treatment.

WHENEVER a considerable population lives in a small area, certain special hygienic and engineering problems arise, particularly the problem of the disposal of wastes. It becomes essential to keep the sewage of the community out of the water supply—as New York does—or at least to take measures to minimize the risk resulting from contamination—as the Lake cities do. Other wastes of community life and of industry must also be disposed of; or must be so treated as to become of commercial value.

Often the product saved from the waste helps to cheapen the material from which it originally came. Butcher's meat would cost even more than it does if the scraps of fat and bone could not be sold to a rendering plant; and soap might be a luxury for the rich only. On an even larger scale the disposal of garbage is a city problem, not only of elimination, protection of health, and esthetics, but also of the recovery of valuable materials in the forms of grease, fertilizer, and such by-products as silver spoons. In all this class of industries—such as rendering plants, garbage disposal establishments, the so-called fish factories on the valuable seashore front, sewage disposal plants, and similar establishments—the great objection and difficulty in the past has been the smell, offensive, penetrating, clinging, and under certain atmospheric conditions carrying for miles.

Recently, in a middle-western city on a misty morning with a light southerly wind, we noticed the odor of a garbage disposal plant a mile and a half away. As the plant was on the edge of the city and the prevailing wind blows from it over a large urban and suburban district, tens of thousands of people are at times incommoded and real estate is depreciated by hundreds of thousands, or perhaps rather by millions, of dollars. Around one New England city a careful estimate of the population inconvenienced by odors from rendering and garbage plants gave a figure approximating 150,000 people. For the whole of the United States the figures must be in the millions of population, and in the hundreds of millions of dollars for depreciated residential property. The problem of the elimination of industrial organic odors is therefore a matter of public importance well worthy of scientific study.

Until recently, however, no attempts to abate this nuisance have effected anything more than a slight mitigation. Complete success has seemed to be almost unattainable. Municipal political campaigns have turned on the issue of closing down plants representing investments of very large sums of money, and the resulting makeshifts in waste disposal have brought with them unesthetic and unsanitary consequences.

Now, however, by fixing attention not upon the material from which the odor comes, but upon the odor itself, that is, the gaseous emanation in the air, and by applying to this emanation chlorine gas by the process to be here described we have, we believe, virtually solved the problem. But before describing further the principles and experiments upon which our discovery and invention rest, it will be well to consider briefly some features of what is known of the sense of smell and the nature of odors.

NATURE OF ODORS

Few subjects are more obscure.[2] The physiology of smell has indeed in the hands of Zwaardemaker in recent years made progress, but much remains unknown. It is an extremely primitive sense possessed by virtually all animal organisms. Often it is the sense to which the chief vital responses of food, escape, and sex are adjusted. Even in man, in whom this sense seems to have retrograded, it is probable that some of the most fundamental instincts—particularly the first and last above mentioned—are more or less subconsciously dependent upon odors. Humboldt reported that certain Peruvian Indians could follow a trail by scent as reliably as a hound. In some persons even very faint odors may induce nausea.

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[1] Received March 11, 1922.

[2] Most of the facts and references here given are quoted from Tigerstedt's "Textbook of Physiology," translated by Murlin, New York, 1906.

The olfactory sense is not, as might be supposed, located in the nasal passages proper, but in the olfactory epithelium or membrane covering only a small part of the septum high above each nostril—a total area of less than a square centimeter. The breath does not therefore pass over this membrane which is innervated by the first or olfactory nerves. The lining of the nasal passages proper is on the contrary innervated by branches of the fifth cranial nerve, and irritation of that membrane therefore causes not a sense of smell, but a tickling which induces sneezing. Usually it is by diffusion into the upper chambers that odorous gases or vapors or emanations reach the olfactory membrane. It is only when the flow of air along the nares is made to vary or move in puffs by sniffing, that puffs of air containing the smell-exciting substances are thrown directly against the membrane.

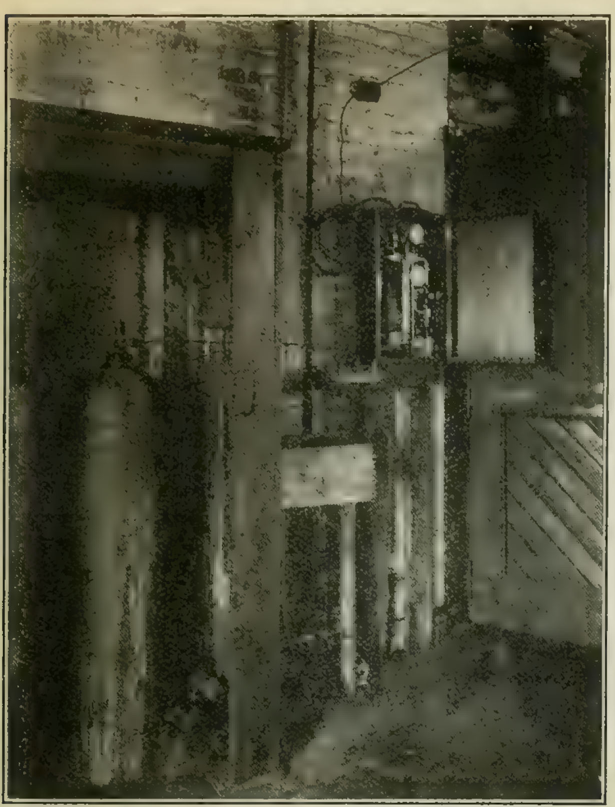

FIG. 1—Apparatus for control of the chlorine injected into vapor-carrying odors at Municipal Garbage Plant, New Bedford, Mass. The well-known control apparatus manufactured by Wallace and Tiernan for chlorinating water supplies has been modified and adapted to the purpose of destroying odors

In part the sense of taste in its common acceptance is dependent upon aromas. The connoisseur of a fine wine could complete his satisfaction only when, after swallowing and drawing a little breath through the mouth, the air bearing the aroma was exhaled through the nose, and was thus diffused to the olfactory membrane.

At one time the character of odoriferous stimulation was supposed to depend upon vibrations of the substances, a mechanical instead of a chemical action. This view seemed to accord with the fact that some substances giving off a strong odor for a long time, such as musk, undergo no loss of weight detectable with the chemical balance. When, however, Berthollet placed camphor in a vacuum over mercury, a lowering of the column finally became perceptible, thus demonstrating a material emanation of the general character of a gas.

Tyndall, in his well-known investigations on the absorption of radiant heat during passage through gases, found that the presence in air of odoriferous substances causes a far larger absorption than pure air. With some substances, such as oil of rose, the absorption increased 36 times, and with oil of anise 372 times.

Another peculiar property of odors is their tendency to adsorption. The use of so-called fixatives, such as balsam, is the basis of the perfumery industry. Some odors hang in clothing almost indefinitely. During a visit to a particularly odorous factory, one of us wore a rain coat of closely woven, smooth cloth. But for two days thereafter, even with constant airing, the sleeve of the coat needed only to be brought near the nose for it to be made clear that the vapor which had condensed on the surface was coming off. Presumably this indicates large molecules or aggregations.

In another observation an attempt was made to draw a large bottle full of the emanations of rotting mixed manure. One end of a rubber tube was inserted in the manure and the other end was connected with an air space in the bottle which was nearly full of water. The water was then syphoned off, and one's nose cautiously applied to the top of the bottle. But instead of an overpowering stench, there was no smell whatever. Presumably all of it had condensed in the tube.

The amounts of some substances mixed with air which are detectable have been determined. In the case of ethyl ether 0.005 mm. per l. of air is perceptible. With camphor a figure of 0.005 is given; for essence of orange, 0.00005. For hydrogen sulfide we have found an amount of less than 0.000001 mg. per l. of air is perceptible although the nose rapidly loses its power to distinguish such an odor. But for the really odorous substances like mercaptan the amounts usually given as perceptible are as little as 0.00000004 mg. per l. of air.

These facts when held firmly under attention afford a conclusion which, now that it has been drawn, needs only to be stated to be almost self-evident. And yet there is between the known facts and this simple conclusion one of those mental obstacles which show how far from being a logical machine the human mind is. The conclusion to be stated and discussed below did not come to us at once and complete through reasoning, but gradually and through experimental study. To state it now as an *a priori* deduction from the facts known about odors is therefore a reversal of the process by which the conclusion was reached.

DEODORANTS

The conclusion is simply this: The total amount of odoriferous substance involved, even when a strong and exceedingly offensive odor is distributed over many square miles of territory, is in absolute amount very small, perhaps only a few grams, or at most only a few pounds or kilograms. Therefore, a process which would effect the mixture with the odoriferous substance of some deodorant agent, such as chlorine, need use only a correspondingly small amount of that agent. This small amount properly applied would give completely the relief urgently demanded, and heretofore largely demanded in vain, by large sections of the population who are compelled to live in regions over which such odors are spread by the winds.

The psychological obstacle above referred to seems to consist in the innate objectivity of the human mind. When looking at any object, one inevitably thinks, not of the light rays reaching the eye, but of the material thing from which these light rays were emitted or reflected. In regard to sounds such as piano music one thinks, not of the vibration in the organ of Corti in the ear, but of the piano string or even more of the fingers of the musician. So in regard to odors, one thinks not of the minute amount of emanation in his nostrils, but of the material source from which that emanation has come. Often this material—be it rotten manure, decayed animal bodies, fermenting garbage, rancid fish scrap, or large volumes of sewage—is present in amounts running into hundreds of tons, or thousands of gallons.

Obviously to act upon the whole of such a mass would involve much machinery and a great quantity of the deodorant; perhaps tons of chlorine would be needed if mixed with such material. There would be a corresponding continual expense, and in some cases an incidental deterioration of the material by the chemical action.

The application of the principle above stated—the action of a comparatively small amount of chlorine upon the gaseous odoriferous emanation from organic material—requires therefore that the deodorant should not be applied to the material giving off the odor. On the contrary, that material in whatever bulk it may be should be handled, dried, digested, aerated—or whatever the process may be—in some closed space from which all the odorous gaseous emanations may be drawn off in a current of air through a duct. Then the deodorant is to be added so as to mix with and act upon the emanation.

For best results the amount of chlorine must be adjusted with considerable quantitative accuracy. The adjustment partakes, as we have found, of the nature of a titration, for if the deodorant is insufficient, some of the emanation escapes, and to the nose a little is often as offensive as much. The nose is not arithmetical. If the deodorant is excessive, it may of itself be a nuisance to the population of the district. Excess of chlorine and the odoriferous substances upon which it can act never exist together for more than a very brief period of time.

It will be seen that the process thus indicated differs in theory fundamentally from that of removing a constituent of a mixture of gaseous substances, such as an odor, by means of an apparatus of the type of an absorber containing solid or liquid substances, such as chloride of lime, or hypochlorite solution, and depending upon the gaseous emanation being blown against the solid or liquid deodorant. Indeed, while odoriferous substances are gaseous in their general nature, they are of such large molecules or aggregations that their rate of vibration or molecular movement is low. Their chance of colliding with solid material or liquid particles or surfaces through their own energy and thus effecting absorption is therefore small. Their contact with stationary absorbing surfaces is correspondingly poor, just as in the absorber of the Army gas mask, the charcoal which absorbed chlorine, phosgene and other gases of small molecular weight, allowed smoke and other suspensions to pass unabsorbed. This may seem to contradict what has been said above regarding the adsorption of smells; but in practice both statements hold true.

In its essentials, therefore, the process which we are here describing depends upon the interaction of odoriferous substances with chlorine when both are in the gaseous or vapor phase. In this condition it is possible, if the mixture is effected and confined in a chamber or duct for the brief period needed for the reaction, to obtain a perfection of mixture and completeness of reaction such that every chlorine molecule finds and exerts its oxidizing action upon a particle of odoriferous emanation. To achieve this object chlorine gas is injected into a duct or chamber through which the odorous vapors are passing. The chlorine is obtained from cylinders of the liquefied gas which are now a regular commercial article. They are sold for bleaching purposes in various industries. Chlorine applied to city water supplies has largely freed us from typhoid epidemics. Indeed it was the question whether or not chlorine could be applied to contaminated and polluted air, without applying it to the material producing the smell, which led to the process here described.

The advantage of applying somewhat the same type of process to air as to water lies in the fact that apparatus for the control and precise adjustment of the flow of chlorine gas for the chlorination of water has already been developed, and is now manufactured and widely used. With a little modification it is adapted to the chlorination of air. But it is to be noted that in theory the chlorination of air is an altogether different thing from the chlorination of water; for in the latter the offensive substances (bacteria, etc.) are aimed at and acted upon, in the former only their emanations.

USE OF CHLORINE

To come now to details: Suppose an industry is located in the midst of a thickly settled district and depends upon that district for its market. Its product is perishable and must be sold quickly. The raw material out of which this product is finally obtained consists of hundreds of tons of the most offensive waste, garbage or offal, which must be stored and then treated on the premises. The expense of chlorinating the whole mass would be enormous and the material would be injured and less salable if chlorinated. Here surely from the standpoint of the neighborhood is a problem in the elimination of odors. The material is handled in a large closed hall or chamber where it may be turned and aerated by hand or machinery; it may be digested with steam in vats or put through a dryer; and once dried even the most offensive material practically loses its power to give off odor until again moist.

The flue from the dryer is led to the chlorinating chamber or duct; the vents from the digestors after passing through condensers are likewise carried to the chlorinating chamber. If the material is merely turned and aerated on the floor or pressed or otherwise treated, the vapors which rise in the carefully closed hall are drawn off through an opening, or a few openings, usually high on the walls or on the ceiling. From this opening a fan, capable of handling several thousand cubic feet of air per minute, draws the contaminated air and drives it through a chamber or along a duct to the final effluent, or in some cases to a stack.

Just beyond the fan a tube of only a few millimeters diameter—it may be a piece of small iron gas pipe—is run into the duct, and there discharges the chlorine gas which is fed into it through the control apparatus from cylinders of liquid chlorine located at some convenient point.

The duct, or chamber, through which the chlorine and odoriferous emanations are discharged must be large enough and must have sufficiently strong vapor currents to effect complete mixture of emanation and deodorant, so as to allow the kinetic energy of the chlorine gas molecules to find and attack every one of the large slow-vibrating particles of emanation. If there is dust, it must be removed by a scrubber before the chlorine is admitted; for only the exterior of the dust particles is acted upon, and unless the chlorine is then in large excess, the odor returns out of the unchlorinated centers of the particles when the dust settles, perhaps a mile or more away from the plant.

At first we feared that when large amounts of ammonia were present, along with the more actively odoriferous substances, the chlorine would be absorbed by reaction with the ammonia and would thus fail of its purpose. Unless sufficient chlorine were added to react or combine with all of the ammonia, the deodorant effect would then be ineffective or incomplete. We have indeed found that there is always a formation of ammonium chloride, as shown by the characteristic mist; but our experience proves that the action of the chlorine upon the odorous emanation is not considerably impeded or reduced even by the presence of such large amounts of ammonia as are exhaled from actively fermenting manure. Even a few pounds of chlorine per day have proved effective in deodorizing a current of stinking air, although this air contained sufficient ammonia to produce an ammonium chloride cloud, and although its volume was in the thousands of cubic feet per minute. Evidently the chlorine molecules—or the intermediate hypochlorite or minute amounts of nitrogen chloride formed by reaction of chlorine with water or ammonia—select the odorous substances as the objects for their particular action.

The presence of water vapor appears to be an essential condition for the efficient action of chlorine; for as has already been intimated the reaction of chlorine is probably first with the water to form hypochlorite, which then reacts to oxidize the odorous substances. It may be, however, that some of these substances belong to the class of unsaturated fatty acids, in which case they would be subject to direct addition reactions with chlorine. From laboratory experiments we have gained the impression that with the vapors from such substances as manure, nearly all of the chlorine finally reaches the form of ammonium chloride.

One of the applications of this process may be particularly instanced. At present the most sanitary method of treating garbage is that of the Cobwell process. By this process the material is mixed with naphtha and cooked in large steam retorts or digestors. It is thus in great part dehydrated, while at the same time the naphtha absorbs the grease, which can then be recovered. The whole process in a well-equipped plant may be kept sufficiently inclosed so that the total amount of odor escaping is very much reduced below that occurring in the commoner process of direct digestion with steam followed by treatment in presses and evaporation. But when the market for grease drops below a certain point and the process is reduced to merely getting rid of the garbage and producing fertilizer, it becomes economically impossible. Evidently at such times, and the present is such a time, it would be most advantageous merely to dry the garbage direct; but to do so produces a quantity of odorous emanation far greater than either of the processes above mentioned. Recently the city of New Bedford, relying upon the chlorination process here described, has installed a direct heat dryer. By this means the raw garbage is dried while the emanation is deodorized in a long duct before being allowed to escape to the outside air. The dried material is quite inoffensive, much lighter and less bulky than before, and capable of sale for fertilizer, or for transportation. Furthermore, it is found that when this material is put through the Cobwell process, of which the city has a plant, only one-third as much time is required as formerly to evaporate off the remaining water and extract the grease. The capacity of the plant is thus virtually tripled.

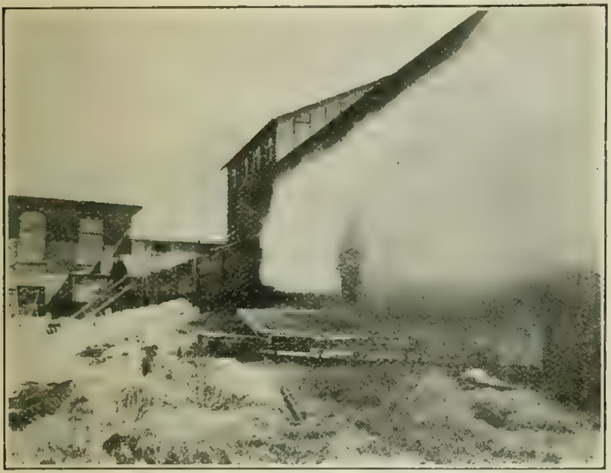

FIG. 2—Vapor discharged through duct from direct heat drier at Municipal Garbage Plant, New Bedford, Mass. Chlorine gas has been introduced into the upper part of the duct and the effluent vapor is entirely deprived of odor

It now becomes possible, therefore, to effect a great simplification and economy in the disposal of the garbage of a large city. In each division of the municipal area there may be a simple drying plant, rendered inoffensive to its neighborhood by chlorination of the effluent vapor. The dried material, which loses more than two-thirds its weight of water, may then be transported to a central plant for extraction of grease, or such other treatment as commercial conditions render profitable.

For some years past chlorine has been used in treating sewage. But large quantities of chlorine are needed even to kill the bacteria, and much larger would be requisite if all the organic matter were to be acted upon. By merely keeping the material enclosed or covered during whatever treatment is given it and chlorinating merely the vapor from it, elimination of aerial nuisance at a comparatively small expense now becomes feasible. In principle the process is so simple that many of the men experienced in the industries concerned have to see it in operation to become convinced of its efficiency. Once installed it runs almost automatically. But for the initial adjustment of quantities it involves a degree of skill and judgment which require a considerable experience to attain.

Finally, as an illustration of the idea of, so to speak, titrating or balancing gas against gas, it may be pointed out that if in another war the wave of chlorine were to be used, as in the first German gas attack in the World War, the liberation of an odorous organic emanation or gas in front of it would make an effective protective barrier.

The Resources of the South

In addressing the General Meeting of the SOCIETY at Birmingham, Mr. William H. Stone, Associate Editor of the *Manufacturers Record*, offered some interesting statistics in regard to the South's resources and present production.

The capital of the South in manufactures in 1920 was nearly $7,000,000,000, and the value of its manufactured products was nearly $10,000,000,000.

The South produces practically all the cotton raised in the United States, or about 60 per cent of all grown in the world. It has the world's largest sulfur deposits and is producing about three-fourths of the world's supply. It has the greatest natural-gas fields known in the world. It has three-fourths of the coking coal area of the United States, and its total coal area is twice as great as that of all Europe, including Russia. It has been estimated that the South has a minimum of 2,600,000,000 tons of red and brown iron ores of commercial grade, not including the clay iron ores of Alabama or the enormous reserves of low-grade red ores. It has an estimated oil reserve of 5,000,000,000 bbls. (about 55 per cent of the country's supply), over 40 per cent of the country's forest area and nearly one-fourth of the standing saw timber, and water-power potentialities sufficient to develop 9,000,000 or more of hydroelectric power.

At present, the South is producing the following approximate percentages of the country's supply:

Bauxite	100	Graphite	60
Fuller's earth	100	Petroleum	57
Turpentine and rosin	100	Mica	51
Sulfur	99	Quartz	50
Phosphate rock	99	Asbestos	48
Crude barytes	92	Lead	45
Aluminium	90	Zinc	42
Carbon black from natural gas	89	Feldspar	40
Natural-gas gasoline	75	Pyrites	33
Commercial fertilizers	66	Talc and soapstone	33
Natural gas	60	Lime	30

The April meeting of the New Jersey Chemical Society, held at Stetter's Hall, Newark, N. J., Monday evening, April 17, proved to be one of the largest ever held by this rapidly growing organization. Prof. W. D. Harkins of the University of Chicago gave a very interesting lecture on "Separation of the Elements Chlorine and Mercury into Isotopes, and the Building of Atoms." A considerable number of the members took part in the discussion following the lecture, which was led by Prof. George B. Pegram of Columbia University and Prof. George Winchester of the State University of New Jersey.

At the business session which preceded the lecture the 1921 officers were unanimously reëlected. The officers are:

President: R. G. WRIGHT *Secretary:* F. D. CRANE
Vice President: C. P. TITUS *Treasurer:* A. R. CULLIMORE
Directors: E. G. JARVIS, S. SKOWRONSKI

After considerable discussion of a resolution introduced by Mr. Williams Haynes, the Society went on record as favoring American valuation in the proposed tariff, in so far as it refers to chemicals, and excepting those products which are already covered by adequate embargo provisions.

Burning of Two Hundred Thousand Pounds of Picric Acid at Sparta, Wisconsin[1,2]

By Charles E. Munroe

National Research Council, Washington, D. C.

On September 28, 1921, at about 3:50 P.M., fire was discovered in Picric Acid magazine No. 263 at the Sparta Ordnance Reserve Depot, Sparta, Wis., which, through wind-blown sparks or burning grass or brush, was communicated to magazine No. 264, situated 800 ft. to the north of magazine No. 263. Within 30 min. after fire was first discovered, the fire in magazine No. 264, with the various grass and brush fires resulting from the original fire, was either entirely extinguished or completely under control, owing to the effective and most courageous behavior of a body of some fifty men who were promptly assembled and efficiently directed by the commanding officer of the Depot.

Sparta General Ordnance Depot

The government reservation known as the General Ordnance Depot at Sparta, Wis., comprises about 14,000 acres, of which about 7000 acres have been utilized for the temporary storage of high explosives and other material. The ground is rolling, and the area includes a number of substantial hills in the form of ridges which so wind about as to form pockets in the lower levels. The soil is sandy and rapidly absorbs water, so that there has been little or no grooving of the pockets by running water. The area is well covered with scrub oak.

Magazines

The magazines were placed in the pockets and on the lower levels and are spaced 800 ft. or more apart, being barricaded by the intervening ridges and the scrub oaks and brush. The magazines in use are of two types, namely, the "Burton portable barracks," which have been adapted to this use, and the "open shed" type. Magazines No. 263 and No. 264, which were on fire September 28, 1921, were of the "open shed" type, and constructed as follows:

Dunnage, 2 in. by 4 in., with 1-in. boards laid across them and close together, were placed on the cleared and leveled ground and the explosives piled on this. The whole was covered by a corrugated asbestos roof supported by 2 in. by 4 in. and 1 in. by 6-in. roof trusses of 20-ft. span on 4 ft. by 4 ft. posts, 6 ft. high at eaves and spaced 8 ft. on center. The roof had an overhang of 2 ft. on all sides.

It is to be recalled that at the declaration of the Armistice the explosives factories of this country were manufacturing at top speed and in increasing number so that in January 1919 there were probably much over 300,000,000 lbs. of smokeless powder and high explosives scattered over the eastern and densely populated states. Owing to the number of disasters, some of great magnitude, and especially that at Morgan, N. J., in October 1918, there arose a widespread demand that these great accumulations be immediately removed from states such as New Jersey, Pennsylvania, and Delaware, and to meet these demands promptly the Ordnance Department was compelled to resort to such temporary expedients as the erection of the open shed type of magazines in locations remote from habitations, such as that at Sparta.

Receipt of Picric Acid

The picric acid magazine No. 263 was received at Sparta during June, July, and August 1919, packed in barrels conforming to I. C. C. Specifications No. 10. Each barrel contained approximately 400 lbs. net dry weight of picric acid and was shipped to Sparta as a "solid inflammable material" containing 10 per cent of moisture. It was accepted by the Ordnance Department, U. S. A., under Specifications No. GE-317, which, among other characteristics, required that "it must be of such a degree of fineness that all shall pass through a 12-mesh screen having openings of 0.058-in. and wire of 0.025-in. diameter." The barrels were stacked in the magazine on end and three high as close together as possible. Originally this magazine contained 217,880 lbs. of picric acid, but deliveries of part of the stock had been made, so that at the time the fire broke out in this magazine there were but 500 bbls. or 200,000 lbs. of picric acid stored there. The deliveries had been made from the center of the pile so that as one approached the magazine on the south or north side an aisle was to be observed between the barrels which space had previously been occupied by some forty-five barrels. The picric acid in this magazine was a part of the surplus war material that had been allotted to the Department of Agriculture for distribution by the Bureau of Public Roads in industrial projects, and it was being conveyed as fast as practicable to the plant of M. J. Connolly & Company within the reservation where it was cartridged and packed under contract with the Bureau of Public Roads.

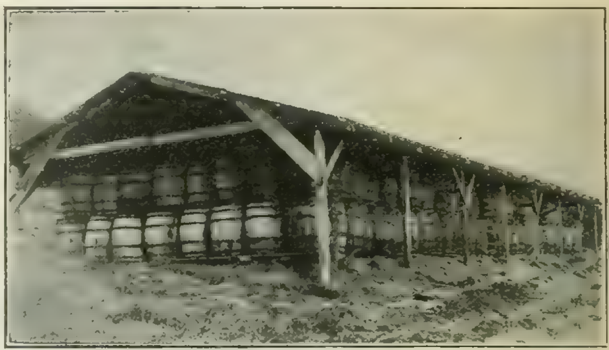

Fig. 1—Open Shed Type of Magazine

Fire Protection

Each magazine was entirely surrounded by a fire break, 50 ft. in width, made by plowing. Barrels of water and buckets

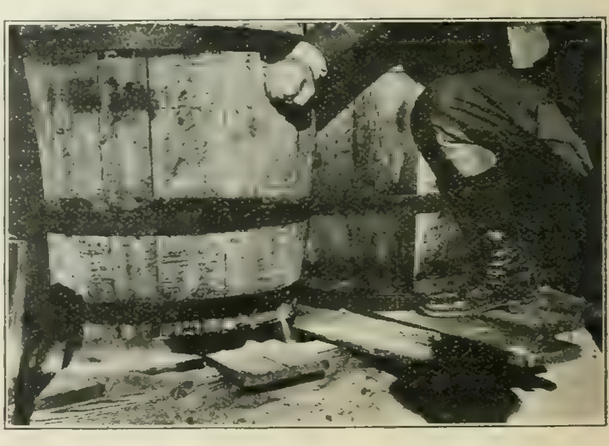

Fig. 2—Sifting Out of Picric Acid

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[1] Received March 16, 1922.

[2] Published by permission of the Chief of the Ordnance Department, U. S. A.

were placed near at hand outside each magazine and supplies of shovels, with which to smother fires by covering them with sandy soil, and brooms, for beating out brush and grass fires, were kept at convenient points in the area. A chemical fire engine was included in the equipment of the depot, and the area was patrolled.

CONDITION OF PACKAGES

It is evident that the picric acid packages, stored as described above in magazines No. 263 and No. 264, were exposed freely to the wind and to an extent directly to the sun. Owing to extreme heat and dryness during the summer, crevices developed between the staves of a number of the barrels, thus permitting the contents to become more or less dried out. To ascertain to what extent this may have occurred three barrels were taken from different positions horizontally and vertically in magazine No. 264 and the moisture content determined in samples taken from the top, middle, and bottom of each barrel. The barrels were taken as follows: (1) south side (first barrel); (2) middle (second barrel); (3) north side (third barrel).

The results of the tests of moisture contents were as follows:

MOISTURE CONTENTS OF EXPOSED BARRELS OF PICRIC ACID

BARREL No.	TOP	MIDDLE	BOTTOM
	PER CENT OF MOISTURE		
1	0.30	0.60	1.20
2	1.47	7.92	8.15
3	2.93	7.40	9.20

As a consequence of this opening up of the staves of the barrels and the drying out of their contents the finely divided material tended to sift out, especially as the barrels were disturbed.

CIRCUMSTANCES OF THE FIRE

Shortly before 3:50 P.M., on September 28, 1921, a 5-ton artillery tractor with two 3-ton trailers attached and carrying a crew of three laborers, engaged in transporting the barrels of picric acid from the magazines to the cartridging plant, approached magazine No. 263 from the southeast, ran along the south side of the magazine, and at about 6 to 8 ft. from it, until it reached the center of the building, when the train was stopped with the tractor turned out so that it was about 10 ft. from the magazine. The wind was at this time blowing from southeast at about 18 mi. per hr. As the train was coming to a stop a man on the trailer discovered fire in or beside the aisle where barrels of picric acid had been taken out and where there was picric acid powder on the boards and grass. He immediately grabbed a shovel and threw sand on the fire but the fire spread so fast and became so hot he abandoned his effort and the crew fled.

At about this time the commanding officer, being then engaged at the loading yard at a distance of about 880 yds. to the south of magazine No. 263, had his attention called to the smoke arising. He at once ordered the fire alarm given, ordered all men present to proceed to the fire, and the fire fighting equipment to be assembled there, and proceeded himself at once by motor truck. On arrival he found about fifty men available, equipped with brooms and shovels, and also the chemical fire engine, but as the fire in magazine No. 263 was then under such headway that it could nct be approached he disposed his force in a semicircle to the north of this magazine to beat out the brush fires, build back fires, and the like, and he proceeded toward magazine No. 264, directing the extinction of grass and brush fires as he proceeded, until when he was within three feet of magazine No. 264, which was of the same construction and arrangement as No. 263, but contained 217,880 lbs. of picric acid, there was a flare and approximately one-fifth of the north section of the magazine burst into flames.

Immediately some fifteen men responded to a call for aid and, entering the magazine, rolled out burning barrels of picric acid and by means of the chemical engine, use of sand, and beating, got the fire under control.

It was then discovered that fire was still burning under the floor of this magazine so other barrels were removed, the flooring torn up, the fire there extinguished, and the magazine and its contents saved.

LOSS AND CASUALTIES

The loss was confined to magazine No. 263 and its contents. The value of the picric acid for its allotted use was estimated at $40,000.

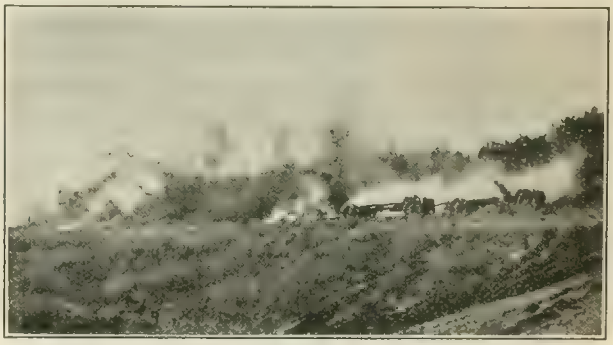


FIG. 3—MAGAZINE NO. 263 DURING THE FIRE

Several of the men fighting the fire were unpleasantly affected by the smoke and fumes which they inhaled, the general complaint being of irritation of the lungs. Two were sufficiently overcome to be taken to a hospital, but it is not improbable that they were suffering also from undue physical exertion. All soon recovered.

SOURCE OF IGNITION

All other sources having been inquired into and eliminated, the source of ignition was found in red-hot carbon forced from the exhaust of the tractor and carried forward by the wind to exposed picric acid. It was found that the approach to the magazine was quite an up-grade through heavy sand and that the tractor came up "in second" with the motor laboring hard.

PHENOMENA OBSERVED

The flames from magazine No. 263 reached a height of 35 to 40 ft. They were extremely quick, sharp, bright, and of a reddish color. The heat was so intense that the metal in the roof and the barrel hoops were melted and a large part completely burned. There is evidence to show that melted iron ran through picric acid, as globules of the metal were found on the sand.

At first there was a great volume of heavy black smoke but as the temperature increased the carbon combustion was more complete. The effect was no doubt modified by the burning of the wood of the barrels and by the water present in the picric acid.

During the burning of magazine No. 263, grass fires were seen to start at points 800 ft. from the magazine and considerably to one side of the line of the wind. This may be accounted for on the theory that large volumes of heated gases from the fire caused whorls of sufficient size and intensity to throw sparks and burning brands a considerable distance to one side.

The intense heat caused such an inflow of air that odors could not be detected by one standing as close to the fire as the heat permitted.

The roar during the fire was so loud that decrepitation or deflagation reports, such as usually accompany the burning of small quantities of picric acid, could not be distinguished. Toward the end of the fire there were occasional small "reports" of about the loudness of a 12-gage shot gun report. These were observed to result from gas confined under unburned picric acid and fallen roof and when these "puffs" occurred picric acid was tossed up 5 or 6 ft. These "puffs" came from beneath the almost completely burned mass.

At magazine No. 264 the smoke immediately on emission from the picric acid was black, though less dense than that from burning crude petroleum, but above this the cloud was of a decided yellow color.

The gas or vapors at this magazine were very pungent, sharply acrid, and very irritating to the mucous membrane of the nose and lungs. It was the men laboring in this magazine who experienced ill effects from the inhalation of these products, which gave rise to choking and strangulation.

ACKNOWLEDGMENT

The writer's sincere thanks are due Major A. J. Stuart, Ordnance Department, U. S. A., for giving him access to the official reports on this event.

The Geography of Electrochemistry[1]

By W. S. Landis

AMERICAN CYANAMID CO., 511 FIFTH AVE., NEW YORK, N. Y.

THE two main applications of the electric current which are of value to the chemist are as a convenient source of heat and as a powerful decomposing agent.

Many factors apply in a comparison of the cost of electric heat with combustion heat. The fact must be considered (and is often overlooked) that electrically generated heat is released in intimate contact with the absorber, at rates balanced against rates of absorption, and in any desired atmosphere. It permits the attainment of high temperatures on a scale unknown to the combustion engineer. The combustion of a ton of high-grade bituminous coal yields approximately the same number of heat units as a kilowatt year of electricity. The losses of heat in flue gases, careless admission of air, incomplete combustion, and radiation from large combustion chambers increase the relative cost of combustion heat. Modern steam power plants operating large units convert the potential energy of coal into electrical energy at thermal efficiencies approximating twenty per cent. This relationship, coupled with the highly efficient conversion of electric energy into usefully applied heat, does not in any sense exclude the steam-electric combination as a competitor of direct firing, and there are many other advantages to help pay the heavier overhead.

In different parts of the world different relationships exist. In parts of Italy favored with water power developments the kilowatt year is produced rather cheaply and many installations have found it cheaper to generate steam by submerging a resistor in a boiler than to burn expensive imported coal. Norway also possesses no coal, but has abundant hydraulically generated power averaging less than $12 per kilowatt year. A plan has actually been worked out for heating all the houses in Bergen from central hot water storage plants, the water itself being electrically heated.

The sole domestic metallurgical fuel of Sweden is charcoal, which is becoming more scarce each year. In the manufacture of pig iron in the blast furnace approximately one ton of charcoal is required per ton of pig iron produced. Of this, one-third is used in chemical reduction of the iron ore and two-thirds are burned up to supply heat for operating the furnace. One-fourth of a kilowatt year per ton of pig iron is sufficient to keep the furnace hot, and when, ten years ago, the price of charcoal rose to a point where a ton of charcoal cost more than three-eighths of a kilowatt year, the old blast furnaces were supplanted by electric furnaces. In other words, when the kilowatt year can be purchased for the same price as two and a half tons of charcoal or coke, the blast furnace becomes obsolete. Norway, Italy, Sweden, and Japan have made the change, and India, Brazil, and our own Pacific States are contemplating the adoption of the electric furnace in the iron industry.

The mere fact that low cost electric power exists somewhere does not always make it cheap. Raw materials, labor, and transportation are often more important factors than electric energy.

Norway possesses cheap power. She has little else in the shape of raw materials and must import supplies. Her labor is scarce, fairly high priced, and of uncertain temperament. She has built up a great nitrogen industry using only air, water, and electricity, and holds a practical monopoly of this type of process.

The carbide and cyanamide processes have failed for several reasons, chiefly because of high cost of imported coal and coke and long hauls on limestone. Her aluminium industry is undergoing a change with the hope of utilizing a local feldspar instead of the usual French ores. Her steel industry has remained small.

Sweden has an electric iron and steel industry of fair proportions, but is handicapped by lack of fuel. Swedish ores will continue to be exported in the face of available electric power for home manufacture.

Germany has developed a considerable electrochemical industry in spite of very limited hydropower. Brown coal efficiently burned under boilers is operating melting furnaces, caustic and cyanamide plants, steel furnace, and other electrochemical processes. She is quite a factor in this industry, certainly leading Europe, and yet has a potential hydroelectric power development of less than one and one-half million horse power.

France possesses great possibilities of hydro development, some of it already available. She possesses the start of a large electrochemical industry, early entering the fields of electrosteel, aluminium, caustic, and fine chemicals. Her coal supply is deficient but other raw materials are plentiful, as are also transportation and labor.

Neither Switzerland nor Italy possesses coal deposits of consequence; yet both are well supplied with water power. Switzerland early started carbide and ferro-alloy production, but demands of the power for manufacturing and transportation will always hold back the electrochemical industry. Italy, on the other hand, is just at the beginning of important developments. Iron, steel, nitrogen fixation, and chemicals will receive a great deal of attention in there.

Russia possesses few important hydroelectric possibilities and will be years recovering from her present political condition.

Finland possesses great hydro possibilities and may develop a small industry, but raw materials are not plentiful and the country lacks all the real fundamentals of a manufacturing community.

England, on steam power, has always been foremost in electrochemical development. She has been the birthplace of many industries which have moved to more favored locations. The rising costs of fuel in England will not revive some of these departed industries, but steam power costs are decreasing slowly with the larger units being developed and the life of the industry as now existent will be prolonged. The metal working industries can easily survive on steam, and electrolytic refining is gaining a strong foothold. The water power resources, while not large, are fair, and are being closely investigated.

Asia is of little present interest to us. Siberia has no remarkable water power possibilities, in fact very meager ones. She has no industrial foundation to build on and may be dismissed from consideration for a long time. It takes more than water and a drop in elevation to start an electrochemical plant.

[1] Abstract of a paper presented before the Cleveland Sections of the American Institute of Electrical Engineers and of the American Chemical Society, Cleveland, Ohio, February 16, 1922.

China has much potential water power but very little organized industry. The development is remote, even though labor and raw materials are plentiful; transportation is most primitive. Manchuria possesses one gas-engine-driven electrochemical plant of Japanese direction.

Japan with her limited supplies of fuel is developing her water powers and possesses several important electrochemical plants. Her engineers are alive to the importance of this industry and more can be looked for, as her hydro resources are not nearly exhausted.

India possesses great water power possibilities. While no electrochemical industry exists at present, the governmental programs for comprehensive development mean that only a few years will elapse before nitrogen fixation and electric iron and steel are well established. Labor is cheap, transportation is fair, and a wide variety of raw materials available though scattered. Home markets await the bulk of the possible products. India probably has more available water power than the United States.

Australia possesses few potential water powers of note and will not figure in the future competition for the home of the industry. The East Indies, on the other hand, with their wonderful power possibilities and raw materials, will some day possess at least a nitrogen fixation industry for home consumption, and metals are not excluded.

Africa need hardly be considered, the few really great water powers being badly located from the electrochemical standpoint. Markets are few, transportation not particularly good, and raw materials, though probably present in rich variety, are undeveloped. Egypt may some day acquire a nitrogen industry, as also South Africa.

The potential water powers of South America are not located conveniently to the sources of raw materials, and the fuel deposits are of questionable value. Transportation is costly, to say the least. This field is, however, being very closely studied and an electric steel industry is a not very remote possibility. Governmental assistance is very likely to assist development. Mexico and Central America will never be factors in our industry, the limited powers being more profitably turned to public service and mining.

Canada possesses many very cheaply developed water powers, but the districts possessing the same contain no fuel. These powers will find their best outlet in the public utility, railroad, and manufacturing fields. Transportation of raw materials and products to market play too great a part in the industry to make for greatly increased developments and the distances are rather great for effective transmission. Niagara power will find increased uses in manufacturing, with electro steel and ferro-alloys as the most important electrochemical industries. A few important hydro developments will at some time make power available on navigable water, and this places Canada in nearly as favorable a position as Norway. Newfoundland is in much the same situation, with power developments close to tide water.

In our own country, its wealth of raw materials, its widely distributed fuels, and its excellent labor and transportation, all have assisted in our electrochemical development, in spite of the fact that really low-priced water power is practically unknown. Our one really great power at Niagara is loaded to the limit of present development with the widest variety of plants. As more and more water is made available to the power plants, not only will local developments increase but transmission will carry the energy to distant fields. Instead of one million horse power we should be generating five million. The great southern power developments will not be available for heavy electrochemical developments in general; they are too expensive considering their distance from market. Public utilities and manufacturing will consume all they can supply in the future. This will not exclude participation in smelting and in mechanical power supply in metallurgical industries. Muscle Shoals will never be another Niagara, no matter how the propaganda reads.

The far West has attracted much attention in our field. Public utilities will always take a large share of these developments, and transportation may some day demand its proportion, for fuel is scarce. The few possible developments which might yield surplus power are handicapped by the fuel and raw material situation, for distances are great in our West. Nevertheless, a steel industry is possible and in fact badly needed. In fact the establishment of any electrometallurgical industry is feasible on certain developments if reasonable transmission to transportation is not antagonized.

The struggle for supremacy is going to be between the United States, Norway, India, China, and Canada. We are far in the lead now, but our rapidly developing manufacturing industries will gradually attract the cheap power now available to the chemical industry, for they are better able to pay the higher price. Many continuous hydro powers can only be inefficiently used in most manufacturing industries, and such should be reserved for the continuously operating furnace processes. But regulation of such kind is to-day impossible in our country.

Society of American Bacteriologists

The Society of American Bacteriologists at a recent meeting in Philadelphia appropriated a fund for the support of a Research Fellowship in pure bacteriology. The Society believes it the duty of bacteriologists to fill the gaps in our knowledge of fundamental principles which are largely due to the fact that the excellent work now being carried on deals largely with practical applications of bacteriology. Applicants for the fellowship must have the degree of B.S. or its equivalent, and the fellow will receive academic credit for the work done from a university of recognized standing. Approximately half his time will be devoted to details connected with the Society's collection of bacteria at the Army Medical Museum. $100 a month is available to cover living expenses. The following committee is in charge of selecting the fellow, supervising the work, approving the problem selected, and passing upon the thesis submitted as the report of the research:

Dr. Victor C. Vaughan, National Research Council, *Chairman*
Captain C. S. Butler, Naval Medical School
Dr. Geo. W. McCoy, U. S. Public Health Service
Dr. John R. Mohler, Bureau of Animal Industry
Mr. L. A. Rogers, Bureau of Animal Industry
Col. Joseph F. Siler, Division of Sanitation, U. S. Army
Dr. Erwin F. Smith, Bureau of Plant Pathology

Bulletin **128** of the Engineering Experiment Station, University of Illinois, "The Ignition Temperature of Coal," by R. W. Arms, makes a study of this problem with the object of determining the influence of the temperature of ignition of the various coals upon the liability to fire while in storage. A discussion is given of what point may actually be designated as the ignition temperature and what factors influence that point, the methods for determining the ignition temperature of different coals, and the results of tests upon the various coals used in this investigation.

At the approaching meeting of the International Union of Pure and Applied Chemistry at Lyons, the matter of organizing the work of the Annual Tables of Constants is to be discussed and an effort made to put it upon a solid financial basis. Plans for providing a certain and sufficient budget for the next five years are in preparation, based upon definite annual contributions from the various countries in the International Union. The confederation of French scientific societies has renewed for 1922 its contribution of 40,000 francs. The total subscription in France during 1921 was 80,000 francs. The National Research Council of Japan has appointed an advisory committee for the Annual Tables, under the chairmanship of Prof. Yukichi Osaka.

CHANDLER MEDAL AWARD

The sixth award of the Chandler Medal was made to Dr. Edgar F. Smith, President of the SOCIETY, at Havemeyer Hall, Columbia University, New York, on the evening of March 2, 1922. The presentation was made by Dr. Chandler himself.

* * *

Samuel Latham Mitchill—A Father in American Chemistry

By Edgar Fahs Smith

The walls of my home office are covered with pictures of past American worthies. Among these are many American chemists. The latter have appealed powerfully to me—so powerfully that within recent years I have made bold to call the attention of students of the history of chemistry to them and their wonderful contributions to this science in days now far gone—in days before the United States were—before your splendid city exhibited any signs of its present magnificence, grandeur, and marvelous activities—when Columbia University, as King's College, dreamed not of its present international character and its unbounded influence in the world of science and field of literature.

But, on turning back to that group of chemists to which reference has been made, arranged in one large panel, and looking down—all of them—upon me, busy in the discharge of my several duties, there is one whose whole life history has interested me exceedingly.

As he was one of yours, as there are in Columbia University several excellent portraits of him, and as one of your Chairs of Chemistry bears his honored name, it occurred to me that, on this occasion, it would be perfectly proper to talk of him to you—to talk of him more particularly in the field of chemistry, outlining what he did for the science in its beginnings here in America, for he was of that group to which are due our admiration and gratitude—a group which I love to think of as the "Fathers of Chemistry in America"—because they really made the science of consequence after Joseph Priestley came to us. In some mysterious way that arch-dissenter inspired them to go forward and develop chemistry along strictly scientific lines.

And yet, as I have returned the look of your representative among the Fathers and recalled his chemical achievements, I have been almost submerged by the consciousness of his boundless contributions to science in general, and to literature in its manifold ramifications, so that as I timidly say, "Permit me, ladies and gentlemen, to present to you Dr. Samuel Latham Mitchill," my own utter insignificance appals me, and stumblingly I add—"the Nestor of American Science;" whereupon, I halt dead, for there pours in on me the knowledge that he was not only a chemist, but that he elaborated and extended the materia medica of our country; that he wrote upon earthquakes; that he disinterred mammoths; that he told of one hundred and sixty-six species of fishes in the fresh and salt waters about your City, thereby "invoking the plaudits of Couvier;" that he carefully investigated the ethnological characteristics of the Red man of America, and translated his war songs out of pure affection for his Mohawk brethren, winning thereby for himself increased celebrity; that he collaborated with other distinguished Americans in the adoption of improved quarantine laws; that he assisted in the preparation of a national pharmacopeia; that he made an exhaustive mineralogical survey (1797) of your State, giving therein later students numerous hints; that he suggested *Fredonia* as a new and more appropriate designation for the United States—a topic that elicited a voluminous correspondence now carefully stored away on the shelves of your State Historical Society; that he engaged in the elucidation of the anatomy of the egg; that he unravelled the nature of meteoric stones, and scrutinized the geology of Niagara; that he made suggestions on the angle of the windmill and discussed with Michaux the beauty of the black walnut for ornamental parlor furniture; that he peered into bivalves and deciphered Babylonian bricks; yet, ready at all times, to argue constitutional law when Kent and Spencer were in the ascendant; that he was the greatest of our ichthyologists, and a true pioneer in geology, but versatile almost beyond belief, for among other things there was scarcely any limitation to his nursery literature. He said, for example:

> You are acquainted with the nursery rhymes commencing "Four and twenty blackbirds?" They abound with errors, added he, and the infantile mind is led astray by the acquisition of such verses. I have altered them this morning:
>
> When the pie was opened,
> The birds they were songless;
> Was not that a pretty dish
> To set before Congress?
>
> I thus correct, said the Doctor, the error that might be imbibed in infancy of the musical functions of cooked birds; and while I discard the King of Great Britain, with whom we have nothing to do, I give them some knowledge of our general government, by specifying our Congress.

These trifles show how intense was his Americanism.

More, much more, of similar nature might be introduced to illustrate the many-sidedness of this remarkable man, possessed of a Herculean memory and keen originality, whose services to the public are best comprehended by reference to the records of State Legislation and Congressional Reports, as he sat in your Legislature and represented your State in Congress and in the United States Senate.

With this partial story of life activities I turn again to the Doctor, and gazing on his smiling countenance remember that, as he wandered in and about the street and lanes of your city, he was five feet ten inches in height, "of comely, rather slender and erect form," with an intelligent, friendly face, an aquiline nose, a gray eye, and full features. His dress was after the fashion of the day, the costume of the times of the Napoleonic Consulate; the blue coat, buff-colored vest, smalls, and shoes with buckles. A man with a heart as well as a head.

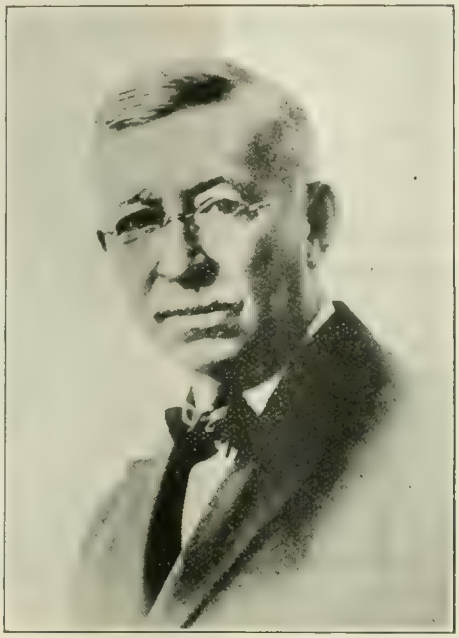
I can see him—this man of unpretending demeanor, of unremitting industry, mingling with all classes—an oracle among his fellowmen, who often affectionately remarked, "Tap the Doctor at any time and he will flow."

PHLOGISTON

But you are eager to hear more specifically of Mitchill as a Father in American Chemistry—so let us begin with his assumption of the Chair of Chemistry in Columbia in 1792. If I recollect correctly, an ancient volume, entitled "Old New York," stated that on assuming this high honor and responsibility "he advanced the scientific reputation of New York by his prompt promulgation of Lavoisier's system of chemistry."

In doing this he abandoned the old theory of phlogiston, and the question may arise as to why he did it, when it is known that he acquired his knowledge of chemistry, in the main, from that grand old master, Joseph Black of Edinboro. Mitchill was but nineteen years of age (1783) when he came under Black's influence—an influence that molded many American minds in the domain of science, and preëminently in that of chemistry. It is worth while to note this fact. In classical learning—in the humanities, in short—it was the Scottish influence—not the English or German—that was imprinted upon American students, and as we come to study the imprint upon the fathers of our science at the beginning it will be discovered to be Scottish—chiefly that of the great Dr. Black, who "saw beauty in a crucible," whose influence upon Benjamin Rush was so pronounced that, medical man though he was, he wrote and published in 1771 his celebrated fasciculus on chemistry—our first American textbook on this subject, and this influence of Black upon Rush may be traced from the latter to Woodhouse, to Robert Hare, to Wolcott Gibbs, and to hosts of others, unconscious presumably of the fact, yet promulgators of the Scottish teachings. Black and Rush abandoned the doctrine of phlogiston in their later years, but Mitchill early forsook it; and, like his distinguished master and all his pupils, assiduously aimed "to render chemistry subservient to the useful purposes of agriculture, art, and hygiene."

It must have been his private thought and experimental work, here at Columbia, which caused him to become the first public champion of the antiphlogistic views in this Western world. This happened in 1792. Priestley had not yet arrived upon American soil, but in June of 1794, when he did land at the Old Battery and was waited upon by the first men of the City, Mitchill was there to extend a cordial, hearty welcome to the discoverer of the greatest of our elements—oxygen—never thinking how intimate their intercourse would be, or how close the ties of friendship between them were to become, and that their correspondence would be frequently cited as "an example of the delicious manner in which argument can be conducted in philosophical discussion."



DR. EDGAR F. SMITH

This brings me to *The Medical Repository* founded by Dr. Mitchill in 1797. It was a journal originally intended to serve medicine, but it became the repository for science in this country in those early days, and through the eighteen years of Mitchill's connection with it. On its pages may be found many of our earliest chemical contributions, and there it was that letters of Priestley and Mitchill on phlogiston were published. From them let us extract a few paragraphs, showing the thought of Mitchill on a subject—phlogiston—upon which Priestley compelled American students of chemistry to think.

Priestley had scarcely settled himself in his American home when he reviewed his experimental work for the purpose of demonstrating the existence of phlogiston. The French Minister Adet answered him in masterful manner. Woodhouse hurled experiment after experiment at his "air castle," and MacLean, of Princeton, followed in two lectures on *combustion* which, in the eyes of the antiphlogistians, were incontrovertible, saying

> From the view which has been given of the different explanations of the phenomena of combustion, it appears that Becher's is incomplete; Stahl's, though ingenious, is defective; the antiphlogistic is simple, consistent, and sufficient; while Dr. Priestley's, resembling Stahl's but in name, is complicated, contradictory, and inadequate.

To this rather pronounced antiphlogistic statement, it might be expected that Mitchill, as a follower of Lavoisier, would fully acquiesce. Such, however, was not the case, for he said:

> While Professor MacLean has acquited himself reputably***** we would advise our readers [of the *Repository*] to beware, even at this time, of too much positiveness, while the experiments of Mrs. Fulhame and Mr. La Marc*****appear to require solution upon the antiphlogistic theory, and reconcilement with it.

And elsewhere in *The Medical Repository* he expressed himself as follows:

> Upon taking a view of the whole controversy*****there are some phenomena which the antiphlogistic theory cannot explain; and that, therefore, Dr. Priestley has some strongholds, from which it will be difficult, if not impossible, to drive him. On the other hand, the advocates of phlogiston are far from being explicit and definite enough in the meaning of their terms, and on that account, seem not perfectly to understand each other, nor to be clearly understood by their opponents.

Here, in the last few words, "seem not perfectly to understand each other," is perceived the thought which subsequently Mitchill developed in his correspondence with Priestley. But young Woodhouse hammered away in his Philadelphia laboratory, obtaining demonstrable proof of the nonexistence of phlogiston, while Priestley sought also experimentally to support himself in his correspondence, to which one must look to obtain Mitchill's mental attitude on this subject, which had become a *burning* question. Priestley failed to shake his opinion because convincing experimental studies supported Mitchill. Yet, as the controversy was waged and grew more and more heated, Mitchill, desirous of preserving among the "Fathers" a friendly spirit, suggested, as previously stated, that their work—the work of all of them—was most satisfactory, but confusion had arisen in terms and naturally, confusion followed in their deductions. Priestley resented this friendly interposition of Mitchill, who replied (1798) to him:

> Finding that*****my attempt to accommodate the disputes *****concerning phlogiston, had not, in your opinion, been successful, I once more beg your indulgence a few moments, while I state some additional reasons to show it will answer as fully as I promised myself,****

and then he reviewed in a most delightful and lucid way many of Priestley's experiments, his own, those of Woodhouse and others which fell into harmony by merely giving to certain words another meaning. He even went so far as to expunge *hydrogene* and substituted *phlogiston* in its stead, arguing that this amendment would render "the history of combustion more easy to be comprehended, and to explain away the differences and difficulties about the principle of inflammability." He also considered *oxygene* a faulty term, and closed by telling Priestley that

> It would give me great satisfaction that we could settle the points of variance on this subject, though even as it is, I am flattered by your allowing my attempt "to reconcile the two theories to be ingenious, plausible and well meant." Yet, after all I have written, I fear you will still think they *cannot* be reconciled; consequently the labour of those who undertake it is thrown away; they toil to no purpose:
>
> In vain, tho' by their powerful art they bind
> Volatile Hermes and call up, unbound,
> In various shapes, old *Proteus* from the *Sea*.

It would carry us too far to present everything that Mitchill did in this celebrated controversy. He continued an antiphlogistian in his experimental work and in his teaching, so that, among the Fathers who established the teachings of the French school on American soil, his position is assured. It was no little thing to have thus contributed to our science in its infancy, and it is particularly noteworthy that Mitchill should have incorporated the new ideas and facts into his lectures, for he was "a teacher of rare attainments and of singular tact in unfolding complex knowledge with analytic power. Few left the lectures without the conviction that an able exponent had enlisted their attention." And it is recorded: "His manner***** attracted the attention of his students by his intelligible language and pleasing elucidations."

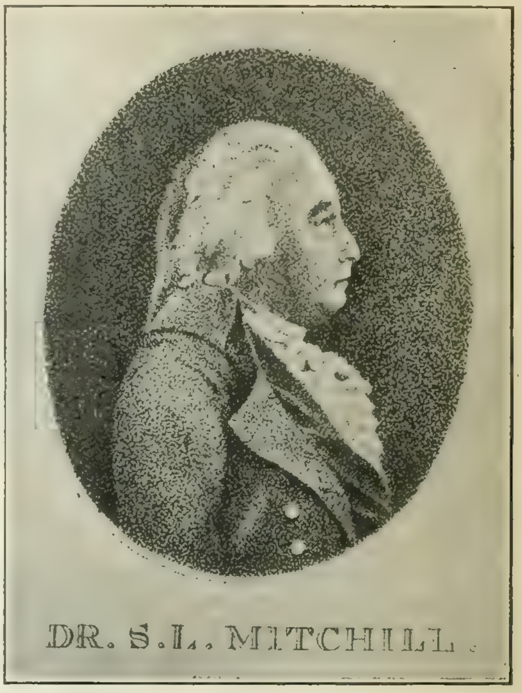
And one will also find with but little search that in addition to his remarkable verbal elucidations, Mitchill also had recourse to demonstrative material, for early in his teaching career he had assembled a "Chemical Museum," evident from this quotation: "The Chemical Museum of Columbia College has been lately enriched by an extensive collection of minerals—the donation of Samuel Owens (1797)."

This allusion to a Chemical Museum in your University promptly brings before me Dr. Chandler and his remarkable Chemical Museum, as well as that rich and stimulating journal—the *American Chemist*—founded and edited by him for years, and also—yes, I must say it—his matchless expository powers as lecturer and teacher—certainly a very legitimate and worthy rival of his earliest predecessor in the Chair of Chemistry at Columbia. Did time permit, many striking resemblances between these two choice exponents of chemistry could with ease be spread before you. My enthusiastic affection for both of them knows no bounds.

Again, among his earliest experiments, Mitchill studied evaporation. His observations on this subject suggest a pioneer effort in physical chemistry, which is not so modern by any means. Now and again the Fathers gave very convincing proofs that they recognized great possibilities in the physicochemical data which arose in their work, but there was a vast, virgin field before them and urgent appeals to use chemistry for the immediate benefit of the country led them to earnest endeavors along these more practical and more apparent lines.

Have you ever seen a pamphlet of eight pages prepared by the Doctor, with the title "Some of the Memorable Events and Occurrences in the Life of Samuel L. Mitchill, of New York, from the Year 1786 to 1827?" It is well worth perusal. He wrote it as an amusement, but it contains a chronological enumeration of one hundred and ninety-two distinct items of achievement in his life career. They are illuminating. Some of them—such as receiving a splendid diamond ring from the Emperor of all the Russias, delivering the annual Phi Beta Kappa oration before Union College, and acting as a committee to receive for and remit to the Greeks of the Morea and elsewhere the money contributed voluntarily by the citizens of the United States, to aid them in their efforts to free themselves from the dominion of the Turks and to establish an independence of their own, clearly demonstrate the sympathetic character of this exemplar of broad human principles and ideas, who loved to tell that he had also evolved a chemical nomenclature and accompanied it with a brilliant explanatory memoir, urging in it that metals in their ductile and malleable state are compounds of a base with hydrogen (phlogiston); and that in their calciform state they consist of a base with oxygen, and contended further that in several there is an intermediate condition, in which there is no union either with hydrogen or oxygen. And this doctrine he extended to nearly all the inflammable bodies.

It was in this chart (1802) that Mitchill declared all matter consisted "of atoms infinitely small, balanced between attractive and repelling powers. These atoms are the materials which constitute the greatest as well as the least of the aggregate and compound bodies in creation*****of these atoms we know nothing but from their effects and properties. Their essence is beyond our researches."



DR. S. L. MITCHILL.

One wonders how the ions and electrons of the present would be viewed by the Doctor.

In the same remarkable document he introduces the term anticrouon, signifying caloric. It is the repelling force. It is present in all substances. It causes the repulsion in the atoms of which bodies consist. It is impossible to conceive of their constitution without taking it into consideration.

There is to be seen in this doctrine (1801) a lurking bit of phlogistonism, which however completely disappears in the succeeding years. Mitchill's mind was speculative in its nature, so it is not surprising that his earliest views should have clung to his later more practical endeavors.

If we could have greeted him in the flesh, extended a fraternal hand, he would probably have charmed us with his intimate knowledge of minerals and perhaps would have entertained us with an account of his tours in search of minerals, and advised us as to how he published an American edition of Phillips' "Mineralogy," giving us in words much of the information he gave in the footnotes of that volume. These are entertaining reading and mark not the dilettante, but the master. He applied chemical analysis to minerals, and, indeed, must have been much occupied in this way, for in letters written while United States Senator, he tells many of his correspondents who impatiently seek knowledge of the constitution of certain material, that in the absence of any laboratory utensils and reagents, they must excuse his inability to assist them until his return to his workshop. Here are his words:

> It would give me great pleasure to undertake what you propose, but I fear it will be impossible in my present situation. I have none of the things*****I am wholly unfurnished with the reagents and the materials requisite in exact experiments***** the actual incompatibility of my present situation with anything like regular analysis could withhold me. At a future day and at a time when I am not surrounded with subjects for *political analysis*, I will respond to your request.

And the national government sought to profit by his chemical knowledge, since there is correspondence from the Secretary of the Navy relative to the unsatisfactory cannon powder on many of the vessels. To which the Doctor answered: "The fault you find with your cannon powder is due to the impurity or adulteration of the saltpetre employed in its preparation." Elaborate directions to eliminate this evil are given by Mitchill, promising that if his course of purification be adopted the product will be strong and effective—"to the annoyance of the enemies of our country."

In this connection also it might be mentioned that in eliminating some of the difficulties encountered by soap makers, Mitchill discovered phosphate of potassium in wood ashes. Indeed, he wrote not a little upon the composition of the latter and announced "*Cinis*—a species of alkaline earth*****which chemists have not as yet noticed in their nomenclature." He defined it as a *peculiar earth* which in his opinion has as good a right to stand conspicuous, and be known and talked of, as either magnesia or lime, potash, or soda; all of which are to be considered as compounds, but retained in the list of simples until their constituent parts can be ascertained by analysis. *Cinis* is the chief component of wood ash.

My dominant thought on reading this declaration was—how carefully did the Doctor examine this wood ash residue? Many such statements in our very early chemical literature have moved me, time and again, to follow up the suggestions, sometimes with surprisingly good results, and again with disappointments, although usually the latter were accompanied by a fuller understanding of the many obstructions and difficulties which lay in the way of the Fathers in performing their analytical experiments. It is altogether likely that those who attempted to unravel the mystery surrounding the wood-ash residues would discover a strange mixture, as did Clemens Winkler when he wrestled with the gnomium of Gerhard Krüss, who believed he had detected this new element in nickel.

Still, it will go uncontradicted that Mitchill knew much about wood ashes and potash. He stubbornly maintained that the latter held oxygen as one of its components, and when Davy isolated potassium from the latter, there were among Mitchill's admirers many who thought that the Doctor's unceasing remarks on potash had given to Davy the hint which led to the experiment that crowned his efforts with success and gave to the chemical world a new and wonderful instrument by which to disclose constitution. And this it became.

Indeed, Felix Pascalis, author (1802) of a celebrated address on chemistry, and a devoted friend of Mitchill, with whom he carried out many important studies, was of those who said: "With the same intuitive penetration Mitchill anticipated those famous results of the experiments made by Sir Humphrey Davy with the galvanic battery upon alkaline earths."

SEPTON

And now we reach a chapter in the experimental work of Mitchill which challenges the most appreciative respect. Very early in his professional career he earnestly thought on the decay of matter. With a mental medical bias, diseases and fevers of all varieties had their origin in the poisons which arose in the decay of organic, nitrogenous matter. This poisonous material Mitchill strove to overcome. He believed it possible through the agency of an element which by union with oxygen gave rise to acidic products which would arrest decay and utterly annihilate the noxious gaseous bodies. For some reason he chose to designate this new principle as *septon*, saying in many places that it really was azote, and when confronted with the knowledge that azote in union with oxygen yields nitrous and nitric acids, he affirmed that azote (nitrogen) preëxisted in the form of *septon*, which seemed to obsess him, for he indited (1797) an elegant and animated ode to it and its annihilating virtues:

Gnomes! ye beheld with pity and with pain
Organic relics strew the fertile plain.

Ye saw, with wondering eyes and rare-drawn breath
Infused the peccant principle of death—

Grim Septon! Armed with power to intervene
And disconnect the animal machine.

Within the great disorganizer lurks
And plans, unseen, his undermining works.

The perusal of these virtues of septon and its happy applications is difficult. One pauses; yes, even doubts and flounders about for an explanation, when all at once he is lifted out of the dilemma and restored to cheery certainty by reading the words of Felix Pascalis:

> This *septon* (of Mitchill) is the *chlore* of Scheele, of Vauquelin, of Fourcroy and of Guyton de Morveau—the element of the boasted *chlorides* so abundantly spread throughout the earth,—

And Mitchill adds to our joy by saying:

> My native acid of Septon is a combination of this base (chlore) with oxygen. It is the same which is the base of oxygenated muriatic acid and which is proved by modern chemists to be an element of extraordinary nature and most disorganizing properties.

In the language of Mitchill it (septon)

> is the universal decomposer*****deleterious to everything animated, but united with alkaline earths it separates and neutralizes putrid compounds, and through the alcalescent medium dissolves, modifies or consumes the unsound matters of contagion and pestilence, or the virus of diseases.

Septon, continues Mitchill, "is a fiend to animal and vegetable life," and he applauded the various chlorides of lime, of potash, of soda and salt to stay the ravages of the pesthouse; to purify from filth, and held that they deserved rank "in materia medica as anti-septics, relieving or curing maladies."

In all this Mitchill clearly assumed the role of a sanitary chemist, and as such must be hailed as the earliest pioneer, whose efforts and discoveries antedated by at least thirty years those proclaimed with so much pride in Europe.

Many of his papers were promptly translated. His correspondence from all parts of the civilized world on this topic became voluminous. Quite frequently does one encounter lines such as these: "Prof. Reich of Erlangen writes that several of Dr. Mitchill's pieces on pestilential fluids have been translated into German." The manner of the obliteration of these fluids naturally follows.

Personally, I feel that these contributions of Mitchill have too long lain unstudied and unannounced. He was a veritable biochemist.

The Fathers of chemistry in America were keen to have their science serve their country. Woodhouse, Seybert, Coxe, Maclean, Mitchill, like many others, made it the central science thus anticipating the later, noble expression of your distinguished President, Dr. Butler, who said a while ago: "Probably no one will dispute the statement that the central science just now—the one that is likely to remain the central science for some time to come, is that many-sided body of knowledge called chemistry."

Further, these "Fathers" were patriots. Mitchill establishing his claim thereto when he "laboured jointly with his patriotic neighbors with mattock and shovel, in the trenches to erect fortifications against the enemy in 1814."

The time, however, has arrived to close this narrative (incomplete as it is) of the achievements of the son of a Long Island Quaker farmer, who as a boy, in prosecuting his studies on long winter nights, when candle light was not allowed him according to his wishes, made a preparation of brushwood and other light fuel, from the flames of which he continued his studies long into the night.

At the period when Mitchill would have entered King's College, that institution, erected to letters, was appropriated to arms, scholastic exercises suspended and the professors dispersed, so that it was under the guidance of Dr. Leonard Cutter, an alumnus of Cambridge (England), that Mitchill acquired an intimate acquaintance with classical literature which constituted one of his delights throughout his subsequent life.

Although, for the sake of medical studies, he eventually did come to New York, he found the College a military hospital, its chambers occupied by the sick and wounded of the British Army, but happily received an opportunity to repair to Edinboro, from which University he won his medical degree in 1786—at twenty-two years of age. His thesis lies before me. It covers twenty-five pages of excellent Latin.

Mitchill's rank was eminent among scientists. Ancient and modern languages were unlocked to him. And often, very often, he would resort to verse to exhibit his affection for favorite sciences. Witness a few lines on the "Nautilus:"

> I saw thee, beauteous form,
> As late I walked the oceanic strand,
> And as my curiosity was warm,
> I took thee in my hand.
> Soon I discovered a terrific storm,
> Which nothing human could command
> Had robbed thee of thy life and cast thee on the sand.

Or that on the "Diamond and the Rose:"

> Those matchless rays the diamond shows,
> With promptness I decline,
> That I may dwell within the rose
> And make its blossoms mine.

Many of the Doctor's most delightful literary contributions and scientific communications have fallen into an unmerited oblivion, but the record of his chemical activities remains and will surely serve as an inspiration for us, followers of his favorite science, to emulate him.

Among popular testimonials of his abilities might be cited his investiture into learned institutions of Europe and of this country, the seals of more than a hundred of such diplomas at home and abroad bearing the name of Mitchill.

A gentleman who lingered at the grave of Mitchill on the day of his funeral (September 7, 1831), not being recognized by the sexton, asked of the latter "whom he had just buried?" "A great character," he answered, "one who knew all things on earth, and in the waters of the great deep."

And on the beautiful monument, marking his last resting place, in Greenwood Cemetery, are cut these words:

> Whether there be knowledge it shall vanish away.
> For we know in part.

SCIENTIFIC SOCIETIES

Methods for the Analysis of Rubber Goods

Recommended by the Committee on Methods of Analysis of the Rubber Division of the American Chemical Society[1]

At the meeting of the AMERICAN CHEMICAL SOCIETY held in Rochester, N. Y., 1921, a Committee was appointed to draw up a standard procedure for the analysis of rubber goods. This Committee suggests the following tentative procedure. It is being published so that all chemists may have an opportunity to make their criticisms. Any criticisms should be sent to the chairman of the Committee as soon as possible, for it is desired to present the procedure in its final form for adoption at the fall meeting in Pittsburgh.

REASONS FOR THE ANALYSIS

ACETONE EXTRACT—If the acetone extraction is made on a vulcanized compound, the acetone removes the rubber resins, the free sulfur, any mineral oils or waxes, and part of any bituminous substances or vulcanized oils that may have been used. The percentage of free sulfur is determined and deducted from the total extract. The corrected figure thus obtained will at times give valuable information regarding the quality of the rubber present. For the best grades of Hevea rubber, this should not exceed 5 per cent of the rubber present. A higher extract may indicate the presence of inferior or reclaimed rubbers.

CHLOROFORM EXTRACT—The chloroform extraction removes a portion of the bituminous substances and serves as an indication of their presence.

ALCOHOLIC-ALKALI EXTRACT—The purpose of the alcoholic-alkali extraction is to detect the presence of rubber substitutes.

FREE SULFUR—The free sulfur is defined as that which is removed during the acetone extraction.

TOTAL SULFUR—This represents the sulfur that occurs in the compound either free or chemically combined.

ASH—The ash is the residue left after ignition and consists principally of the nonvolatile mineral fillers, together with their reaction products with sulfur.

SULFUR IN ASH—The sulfur in ash consists of the sulfur from the mineral fillers, and also part of the sulfur that was with the rubber, but which during ignition enters into combination with one or another of the mineral fillers.

SPECIAL DETERMINATIONS—Special methods are given for the analysis of compounds that contain glue, carbon, antimony, and waxy hydrocarbons.

RUBBER—Up to the present time no accurate method has been devised for the direct determination of the amount of rubber present in a vulcanized compound. For this reason the indirect method outlined below is recommended.

PREPARATION OF SAMPLE

1—Before preparing a sample for analysis, the analyst shall, by inspection, assure himself that it has not been contaminated. The sample shall be prepared by taking pieces from various parts of the original sample and separating them from foreign matter.

2—Either grind to the required fineness on a rubber mill or cut with scissors so as to pass a No. 14 sieve.

3—Hard rubber should be prepared by rasping with a coarse file, cleaning with a magnet, and passing through a No. 14 sieve.

4—Crude, reclaimed, or unvulcanized rubber shall be sheeted out very thin on an experimental mill and shall be rolled in holland or other cotton cloth to prevent the sample from sticking. If no mill is available, the sample shall be cut with scissors as fine as possible.

5—Samples of rubberized cloth shall be prepared by cutting into pieces, 1.5 mm. square, and then mixing well.

6—Cements: Evaporate to dryness and analyze the residue as an unvulcanized sample. Steam-distil a separate sample if examination of the solvent is desired.

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[1] Mr. S. Collier, *Chairman*, Bureau of Standards, Washington, D. C.; Prof. H. E. Simmons, Municipal University of Akron, Akron, Ohio; Mr. Wm. B. Weigand, Ames, Holden, MacCready, Ltd., Montreal, Can.; Mr. A. H. Smith, Rubber Service Laboratories Co., Inc., Akron, Ohio; Mr. E. W. Oldham, Firestone Tire & Rubber Co., Akron, Ohio; Mr. H. B. Pushee, General Tire & Rubber Co., Akron, Ohio; Mr. A. H. Flower, Falls Rubber Co., Cuyahoga Falls, Ohio; Mr. F. J. Dugan, Goodyear Tire & Rubber Co., Akron, Ohio.

Reagents

7—The acetone shall be chemically pure and shall be freshly redistilled over anhydrous sodium carbonate, using the 56° to 57° C. fraction.

8—The alcoholic-alkali solution shall be of normal strength. It shall be made by dissolving the required amount of alkali in the smallest quantity of hot distilled water and adding this to specially purified alcohol, which is prepared as follows:

> Dissolve 1.5 g. of silver nitrate in 3 cc. of water, and add it to 1000 cc. of alcohol. Dissolve 3 g. of alkali in the smallest amount of hot water, cool, add it to the alcoholic-silver nitrate solution, and shake thoroughly. Allow the solution to stand for at least 24 hrs., filter, and distil. (Alcohol denatured with 10 per cent by volume of methanol may be used in place of ethyl alcohol.)

9—The nitric acid-bromine reagent shall be prepared by adding a considerable excess of bromine to concentrated nitric acid and shaking thoroughly. It can be used immediately.

10—The zinc-nitric acid solution is made by adding 200 g. of zinc oxide to 1000 cc. of concentrated nitric acid.

11—Barium chloride solution shall be made by dissolving 100 g. of crystallized barium chloride in 1 l. of distilled water, and adding 2 to 3 drops of concentrated hydrochloric acid. If there is any insoluble matter or cloudiness, the solution shall be heated on the steam bath over night and filtered. Care should be taken not to add more acid than the amount specified.

12—Standard 0.1 *N* potassium permanganate solution is made as follows:

> Dissolve approximately 3.1 g. of potassium permanganate in 1 l. of water, and after about 1 mo. filter the solution through an ignited asbestos pad. Weigh out 0.25 g. of pure metallic antimony and transfer it to a 600-cc. Erlenmeyer flask. Add 12 to 15 cc. of concentrated sulfuric acid, 10 to 12 g. of potassium sulfate, and heat until all the antimony is dissolved. Dilute to 250 cc. with water, add 20 cc. of concentrated hydrochloric acid, cool to 10° to 15° C., and titrate with permanganate solution until a faint pink color is obtained.

$$1 \text{ cc. of } 0.1\ N\ \mathrm{KMnO_4} = \frac{\text{Wt. of metallic antimony}}{\text{Cc. of permanganate}} = \text{Grams of antimony} = \text{Sb}$$

13—Starch iodate paper is prepared by impregnating filter paper with a solution obtained by heating 2 g. of starch with 100 cc. of water and, after solution, adding 0.2 g. of potassium iodate dissolved in 5 cc. of water.

14—Prepare a Gooch crucible in the following manner: Amphibole asbestos is cut fine with shears, digested with 10 per cent caustic soda solution, washed with water and then digested with concentrated hydrochloric acid for a few hours on the steam bath. After it has been washed comparatively free from acid by decantation, the asbestos is shaken up with water and the resulting mixture is used in preparing the pads. The Gooch crucibles should be ignited, and are then ready for use.

15—The purity of all materials shall be checked and determined by blank analyses.

Methods of Analysis

16. SPECIFIC GRAVITY—This shall be determined by the use of a pycnometer, using alcohol in place of water, to eliminate the errors due to air bubbles.

A = Wt. of pycnometer filled with alcohol.
B = Wt. of pycnometer filled with sample and alcohol.
C = Wt. of sample.

$$\text{Sp. gr.} = \frac{C}{C-(B-A)} \times \text{Sp. gr. of alcohol.}$$

17. ACETONE EXTRACT—The extracting apparatus used here and for other extractions shall be of the type similar to that shown in This Journal, 9 (1917), 314. The flask shall be heated so that the period of filling an empty siphon cup with acetone and completely emptying it will be between 2.5 and 3.5 min.

Place 2 g. of rubber in a thimble made by folding a filter paper so that it will fit in the extraction cup, which is suspended in a weighed extraction flask. Extract the sample continuously for 8 hrs., unless the solution in the thimble is still colored at the end of that time, when the extraction shall proceed for a further period of 4 hrs. or longer. For hard rubber the extraction period shall be a minimum of 72 hrs. Carefully note all characteristics of the acetone extract, both when hot and cold. Distil off the acetone on the steam bath at as low a temperature as possible. Loss of extract by bumping can be avoided by means of a gentle current of air or by slightly inclining the flask.

Care must be taken to avoid allowing the flasks to stand on the steam bath after the solvent has been removed, because appreciable quantities of free sulfur may be lost by so doing. Dry the extraction flask and contents in an air bath for 1 hr. at 70° C., cool, and weigh. Call the residue "Acetone Extract, Uncorrected."

$$\text{Percentage of acetone extract, uncorrected} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

Save the rubber sample and keep for future determinations.

18. CHLOROFORM EXTRACT—The rubber sample (Paragraph 17), without removing the acetone from it, is suspended in a second weighed extraction flask and extracted for 4 hrs. with chloroform. Care should be taken that any small particles of rubber, which are often carried down into the extract, are filtered off. Evaporate off the solvent and dry for 1 hr. at 70° C., cool, and weigh. The color of the chloroform solution should be recorded. Reserve the rubber for extraction with alcoholic-alkali.

$$\text{Percentage of chloroform extract} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

19. ALCOHOLIC-ALKALI EXTRACT—Dry the rubber from the chloroform extraction at about 70° C. to remove the chloroform, transfer to a 200-cc. Erlenmeyer flask, add 50 cc. of alcoholic-alkali solution, and heat under a reflux condenser for 4 hrs. Filter into a 250-cc. beaker, wash with two portions of 25 cc. of boiling alcohol; then with three 25-cc. portions of boiling water, and evaporate the filtrate to dryness. Use about 75 cc. of distilled water to transfer the residue to a separatory funnel. Add a few drops of methyl orange and acidify the solution with 10 per cent hydrochloric acid. Extract with four 25-cc. portions of ether, unless the fourth portion should be colored, when the extraction must be continued until no further quantity can be removed. Unite the ether fractions and wash thoroughly with distilled water until free from acid (two washings are generally sufficient). Filter the ether solution through a plug of absorbent cotton into a weighed flask, wash with ether, evaporate, dry for 1 hr. at 70° C., cool, and weigh.

$$\text{Percentage of alcoholic-alkali extract} = \frac{\text{Wt. of sample}}{\text{Wt. of extract}} \times 100.$$

20. FREE SULFUR—Add to the flask containing the acetone extract, uncorrected (Paragraph 17), 50 to 60 cc. of distilled water and 2 to 3 cc. of bromine, and cover with a watch glass. (If the acetone extract indicated a large amount of free sulfur, the amount of bromine used may be increased.) Allow the flask to stand 0.5 hr. on the side of the steam bath, then heat cautiously over the direct steam bath until the solution is practically colorless, filter into a 250-cc. beaker, and dilute to about 175 cc. with distilled water. Precipitate with barium chloride and determine in the usual manner, taking the proper precautions to prevent the reduction of the barium sulfate during the ignition.

$$\text{Percentage of free sulfur} = \frac{\text{Wt. of } \mathrm{BaSO_4} \times 0.1373}{\text{Wt. of sample}} \times 100.$$

21. TOTAL SULFUR—Place 0.5 g. of rubber in a porcelain crucible of about 75-cc. capacity, add 15 cc. of the nitric acid-bromine mixture, cover the crucible with a watch glass, and let

it stand for 1 hr. in the cold. Heat for an hour on the steam bath, remove the cover, rinse it with a little distilled water, and evaporate to dryness. Add 3 cc. of nitric acid, cover, warm a short time on the steam bath, then let it cool. Carefully add in small portions, by means of a glass spatula, 5 g. of sodium carbonate (weighed to 0.5 g.). The watch glass is to be raised only high enough to permit the introduction of the spatula. The carbonate is allowed to slide down the side of the crucible and is not dropped directly into the acid. Rinse the watch glass with 2 or 3 cc. of hot distilled water and stir the mixture thoroughly with a glass rod. Digest for a few minutes, spread the mixture half way up the side of the crucible to facilitate drying, and dry on a steam bath. Fuse the mixture by heating over a sulfur-free gasoline flame.

Place the crucible in an inclined position on a wire triangle and start the ignition over a low flame. The tendency for the rubber to burn too briskly is controlled by judicious use of the stirring rod with which the burning portion is scraped away from the rest. When part of the mass is burned white, a fresh portion is worked into it, and so on until all of the organic matter is destroyed. It is necessary to hold the edge of the crucible with tongs. Toward the last half of the operation the flame should be increased somewhat, but it is never necessary to heat the crucible to redness. With care a crucible can be used for at least ten or twelve fusions.

After a fusion, allow the crucible to cool, place it in a 400-cc. beaker, add sufficient distilled water to cover the crucible (about 125 cc. are required), and digest on the steam bath for 2 hrs., with occasional stirring. If the filtration cannot be made in the same day, do not add the water, but allow the fusion to stand over night.

Filter the solution into a covered 400-cc. beaker containing 5 cc. of concentrated hydrochloric acid, and wash the residue thoroughly with hot water. (A qualitative test for barium sulfate can be made on the residue.) Now complete the acidification of the filtrate and washings and add 2 cc. of concentrated hydrochloric acid in excess. Cover the beaker and heat the solution on the steam bath. The total volume of the solution should not exceed 300 cc. The solution must be acid to Congo paper in order to insure the complete destruction of the carbonates. Precipitate with barium chloride and determine the sulfur in the usual manner.

$$\text{Percentage of total sulfur} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

22. ALTERNATIVE METHOD—Place a 0.5-g. sample in a 500-cc. Erlenmeyer destruction flask (Pyrex glass). Add 10 cc. of zinc oxide-nitric acid solution and whirl the flask rapidly to moisten the sample thoroughly. If convenient, the mixture may be allowed to stand over night at this point. By so doing the sample becomes partly decomposed; this permits the addition of fuming nitric acid with no danger of ignition of the sample. Add 15 cc. of fuming nitric acid and whirl the flask rapidly to keep the sample immersed to avoid ignition by too rapid oxidation. With some samples it will be found necessary to cool the flask under a stream of tap water.

When the solution of the rubber is complete, add 5 cc. of saturated water solution of bromine, and slowly evaporate the mixture to a foamy sirup. (For the determination of total sulfur in unvulcanized mixtures use 3 cc. of bromine in place of bromine water.)

If particles of organic matter remain at the end of the evaporation, add a few cc. of fuming nitric acid and reëvaporate as before. Cool, and add a few crystals of potassium chlorate to assist in the oxidation of the sulfur and the decomposition of any nitrates.

Place the flask on asbestos gauze and evaporate the mixture to dryness over a Tirrill burner. Then bake the mixture at the highest temperature of the burner until all nitrates are decomposed and no more nitrogen peroxide fumes can be detected. (Care should be taken to insure uniform penetration of the heat throughout the contents of the flask and to remove the flask as soon as the "baking" is complete.) When the baking is complete, cool the flask, add 50 cc. of (1 : 6) hydrochloric acid and heat until solution is complete. (In case the original mixture contains barium salts, they will be precipitated at this point. If litharge is present in the mixture, lead salts, not otherwise removed, will be eliminated in the final washing with boiling water.) Filter the solution, dilute to 300 cc., precipitate with barium chloride, and determine the sulfur in the usual manner.

$$\text{Percentage of total sulfur} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

23. ASH—Wrap a 1-g. sample in a filter paper, extract with acetone for 4 hrs., and transfer to a weighed, approximately 50-cc. porcelain crucible. Distil off the rubber over a very small flame, not allowing it to catch fire, and ignite until burnt clean, cool, and weigh.

$$\text{Percentage of ash} = \frac{\text{Wt. of ash}}{\text{Wt. of sample}} \times 100.$$

24. SULFUR IN ASH—Add 3 cc. of nitric acid-bromine mixture to the ash (Paragraph 23), cover with a watch glass and heat for 1 hr., remove the cover, rinse it with a little distilled water, and evaporate to dryness. Complete the determination of sulfur as described under Paragraph 21.

$$\text{Percentage of sulfur in ash} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

Save the insoluble residue after filtering the solution of the fusion mixture in water for testing according to Paragraph 25.

25. BARIUM SULFATE—The barium sulfate is calculated from the barium in the ash, which is determined as follows: Filter off the insoluble matter after the fusion and extraction in Paragraph 24, wash back into the original beaker with hot water, dissolve the residue in the beaker and any traces on the filter paper with hydrochloric acid, and heat the solution on the steam bath. Filter through the same filter as before and wash thoroughly with hot water. Nearly neutralize the solution with ammonium hydroxide, leaving it slightly acid. Saturate the solution with hydrogen sulfide in the cold, and when the lead sulfide has settled, filter into a 400-cc. beaker and wash thoroughly. The total volume should be not over 200 cc. Precipitate with 10 per cent sulfuric acid and determine the sulfur in the usual manner. Barium sulfate determined above is assumed to have been added as such. Obviously, if barium carbonate is used, it must be determined in order that an undue correction will not be made.

$$\text{Percentage of sulfur as barium sulfate} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

26. TOTAL ANTIMONY—When a qualitative test indicates that antimony is present, weigh out a 0.5-g. sample, and transfer to a Kjeldahl flask, add 25 cc. of concentrated sulfuric acid and 10 to 12 g. of potassium sulfate, place a funnel in the neck of the flask, and heat until the solution becomes colorless. Cool and wash the funnel, dilute the solution to 100 cc. with water, and transfer to a 400-cc. beaker, dilute to 250 cc. with hot water, and precipitate the antimony with hydrogen sulfide. Filter and transfer the precipitate to a Kjeldahl flask, add 15 cc. of concentrated sulfuric acid, 10 to 12 g. of potassium sulfate, and heat as described above until the solution is colorless. Wash the funnel, dilute the solution to 100 cc. with water, add 1 to 2 g. of sodium sulfite, and boil until all the sulfur dioxide is driven out. This is shown when no blue color is obtained with starch iodate paper. Add 20 cc. of concentrated hydrochloric acid, dilute to 250 to 275 cc. with water, cool to 10° to 15° C., and titrate with standard 0.1 *N* permanganate solution until a faint pink color is obtained. If iron is found to be absent, it is not

necessary to precipitate the antimony with hydrogen sulfide, and the second heating in a Kjeldahl flask can be eliminated.

$$\text{Percentage of antimony} = \frac{\text{Sb (Paragraph 12)} \times \text{cc. of permanganate}}{\text{Wt. of sample}} \times 100.$$

27. ANTIMONY IN THE ASH—This is determined in the ash of a 1-g. sample. Transfer the ash to a 600-cc. Erlenmeyer flask, add 12 to 15 cc. of concentrated sulfuric acid and 10 to 12 g. of potassium sulfate, and boil until solution is complete. It may be necessary to warm part of the sulfuric acid in the crucible to transfer any adhering particles to the flask. Rinse with the remaining portion of acid. Then complete the determination as described in Paragraph 26.

$$\text{Percentage of antimony in ash} = \frac{\text{Sb(Paragraph 12)} \times \text{cc. of permanganate}}{\text{Wt. of sample}} \times 100.$$

28. FREE CARBON—Extract a 0.5-g. sample for 8 hrs. with a mixture of chloroform and acetone in a volume ratio of 2 to 1. Transfer the sample to a 250-cc. beaker and heat on the steam bath until it no longer smells of chloroform. Add a few cc. of concentrated nitric acid and allow to stand in the cold for about 10 min. Add 50 cc. more of hot concentrated nitric acid, taking care to wash down the sides of the beaker, and heat on the steam bath for at least 1 hr. At the end of this time there should be no more bubbles or foam on the surface. Pour the liquid while hot into the crucible, taking care to keep as much as possible of the insoluble material in the beaker. Filter slowly with gentle suction and wash well by decantation with hot concentrated nitric acid. *Caution: Empty the filter flask.* Wash with acetone and a mixture of equal parts of acetone and chloroform until the filtrate is colorless. Digest the insoluble material, which has been carefully retained in the beaker, for 30 min. on the steam bath with 35 cc. of 25 per cent sodium hydroxide solution. This treatment with alkali can be omitted if silicates are absent. Dilute to 60 cc. with hot distilled water and heat on the steam bath. Filter the solution of alkali and wash well with hot 15 per cent sodium hydroxide solution. Test for the presence of lead by running some warm ammonium acetate solution, containing an excess of ammonium hydroxide, through the pad into a solution of sodium chromate. If a yellow precipitate appears, the pad must be washed with the ammonium acetate solution until the washings no longer precipitate the sodium chromate solution.

Next wash the residue a few times with hot concentrated hydrochloric acid and finally with warm 5 per cent hydrochloric acid. Remove the crucible from the funnel, taking care that the outside is perfectly clean, dry it in an air bath for 1.5 hrs. at 110° C., cool, weigh, burn off the carbon at a dull red heat, and reweigh. The difference in weight represents approximately 105 per cent of the carbon originally present in the form of lampblack or gas black.

$$\text{Percentage of free carbon} = \frac{\text{Wt. of crucible with carbon} - \text{wt. of crucible after ignition}}{1.05 \times \text{wt. of sample}} \times 100.$$

29. DETECTION OF GLUE—Heat approximately 5 g. of ground sample, with enough water to cover it, for 1 hr. on the steam bath, cool, filter, and pour it slowly into a 1 per cent solution of tannic acid. If a permanent cloudiness, however slight, appears, glue is present.

30. NITROGEN CALCULATED AS GLUE—Extract a 2-g. sample for 8 hrs. with a mixture of chloroform and acetone in the ratio of 2 to 1. Remove the solvents from the sample and transfer the latter to a 750-cc. Kjeldahl flask. Add 25 to 30 cc. of concentrated sulfuric acid, 10 to 12 g. of sodium sulfate, and about 1 g. of copper sulfate. Place the flask on the Kjeldahl digesting apparatus. Heat gently until the first vigorous frothing ceases, then raise the heat gradually until the liquid boils. Continue the boiling until the solution becomes clear. Allow the flask to cool, dilute carefully with 150 cc. of water, and allow to cool. Add 100 cc. of 50 per cent sodium hydroxide solution, pouring it carefully down the side of the flask, so that it does not mix immediately with the acid solution. Add about 1 g. of granulated zinc to prevent bumping and a piece of paraffin the size of a pea to diminish frothing. Connect the flask quickly with a condenser, the delivery tube of which dips into a 500-cc. Erlenmeyer flask, containing 50 cc. of 0.1 *N* sulfuric acid diluted to about 100 cc. Carefully swirl the flask to mix the contents and start to heat gently, increase the flame as the danger of foaming over diminishes, and finally boil briskly until about one-half of the liquid has passed over into the receiver. Add methyl red solution and titrate the excess acid by means of 0.1 *N* sodium hydroxide solution. A blank determination should be made.

$$\text{Percentage of nitrogen as glue} = \frac{100\ (\text{Cc. } H_2SO_4 \times \text{normality} - \text{cc. NaOH} \times \text{normality})\ (0.014)\ (5.56)}{\text{Wt. of sample}} =$$
$$(\text{Cc. of } H_2SO_4 \times \text{normality} - \text{cc. NaOH} \times \text{normality}) \times 3.892.^{[1]}$$

31. UNSAPONIFIABLE MATTER—If this determination is made the free sulfur shall be determined on a separate 2-g. sample.

Add to the acetone extract (Paragraph 17) 50 cc. of *N* alcoholic-alkali solution, heat on the steam bath under a reflux condenser for 2 hrs., remove the condenser, and evaporate to dryness. Transfer to a separatory funnel, using about 100 cc. of water, add 25 cc. of ether, and shake. Allow the two layers to separate thoroughly, then draw off the water layer. Continue the extraction of the water layer with fresh portions of ether until no more unsaponifiable matter is removed, unite the ethereal layers, and wash with distilled water. Transfer the ether to a tared flask, distil off the ether, dry 1 hr. at 70° C., cool, and weigh.

$$\text{Percentage of unsaponifiable matter} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

32. WAXY HYDROCARBONS—To the unsaponifiable matter (Paragraph 31) add 50 cc. of absolute alcohol, and heat on the steam bath for 0.5 hr. Let the flask stand in a mixture of ice and salt for 1 hr. Filter off the separated waxy hydrocarbons on filter paper, by applying a gentle suction. Wash with alcohol (95 per cent will do), which has been cooled in an ice-salt mixture. The funnel should be surrounded by a freezing mixture.

Dissolve the precipitate from the filter paper with hot chloroform, and catch the solution in a weighed 100- to 150-cc. beaker. Wash the flask with hot chloroform, which is added to the same beaker, in order to include any insoluble matter adhering to the walls of the flask. Evaporate off the solvent, dry the residue for about 1 hr. at 70° C., cool, and weigh.

$$\text{Percentage of waxy hydrocarbons} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

CALCULATIONS

33—Percentage of organic acetone extract = percentage of acetone extract, uncorrected − percentage of free sulfur.

34—Percentage of acetone extract, corrected = percentage of organic acetone extract − percentage of waxy hydrocarbons.

35—Percentage of sulfur as antimony trisulfide = percentage of total antimony $\times \frac{S_3}{Sb_2}$ = percentage of total antimony × 0.400.

36—Percentage of total antimony as trisulfide = percentage of total antimony $\times \frac{Sb_2S_3}{Sb_2}$ = percentage of total antimony × 1.400.

37—Percentage of total sulfur, corrected = percentage of total sulfur − percentage of sulfur as barium sulfate − percentage of sulfur as antimony trisulfide.

38—Percentage of ash, corrected = percentage of ash − percentage of sulfur in ash − percentage of antimony in ash.

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[1] Simplified formula when a 2-g. sample is used.

39—Percentage of rubber hydrocarbon = 100 − the sum of the following percentages:

Organic acetone extract
Chloroform extract
Alcoholic-alkali extract
Total sulfur, corrected
Ash, corrected
Carbon
Glue
Total antimony as trisulfide

40—RUBBER AS COMPOUNDED—Percentage of rubber hydrocarbon plus 5 per cent of its weight is taken as "rubber as compounded," except when the sum of the percentages of the acetone extract, corrected, chloroform extract, and alcoholic-alkali extract is less than the figure represented by the arbitrary 5 per cent, as in many high-grade compounds. Percentage of rubber as compounded is then: Percentage of rubber hydrocarbon plus the sum of the percentages of the organic acetone extract, the chloroform extract, and the alcoholic-alkali extract.

41. RUBBER BY VOLUME—Percentage of rubber by volume =

$$\frac{\text{Percentage of rubber as compounded (Paragraph 40)} \times \text{sp. gr. of compound}}{0.94 \text{ (taken as the average sp. gr. of crude rubber)}}.$$

42—Ratio of organic acetone extract =

$$\frac{\text{Percentage of organic acetone extract}}{\text{Percentage of rubber as compounded}} \times 100.$$

43—Ratio of sulfur to rubber =

$$\frac{\text{Percentage of total sulfur, corrected}}{\text{Percentage of rubber as compounded}} \times 100.$$

STATEMENT OF RESULTS

PER CENT
Organic acetone extract
Waxy hydrocarbons
Chloroform extract
Alcoholic-alkali extract
Free sulfur
Total sulfur, corrected
Ash, corrected

PER CENT
Sulfur as barium sulfate
Total antimony
Sulfur as antimony trisulfide
Carbon
Glue
Rubber hydrocarbon
Rubber by volume

Ratio of acetone extract to rubber
Ratio of sulfur to rubber
Specific gravity

The American Leather Chemists Association

The American Leather Chemists Association will hold its 19th Annual Meeting at Bigwin Inn, Lake of Bays District, Ontario, Canada, on June 21 to 23, inclusive.

The following papers are already included on the program: "The Mode of Occurrence of Tannin in the Living Cell," by Prof. F. E. Lloyd, of the Department of Botany, McGill University, Montreal; "The Swelling of Gelatin," by C. R. Smith, of the Bureau of Chemistry, Washington, D. C.; "The Science of Curing," "The Practice of Curing," and "The Bacteriology of the Fresh Hide," by the Leather Research Laboratory of the Tanners' Council, Cincinnati, Ohio; "A Layman in Research," by F. M. Moffat, Chairman of the Tanners' Research Committee; "The Influence of Atmospheric Humidity on the Strength and Stress of Leather" and "The Preservation Effect of Oils and Greases on Leather," by the Bureau of Chemistry, Washington, D. C.; "Syntans and Mixture of Syntans with Vegetable Tans," by S. Kohn; "The Distribution of Grease in Leathers," by L. Balderston, and "Time Reduction in the Tanning Process," by R. O. Phillips. It is expected that several prominent members of the British Society of Leather Trades Chemists will contribute articles to be read at the meeting.

Information in regard to hotel rates, train schedules, railway rates, etc., may be obtained by communicating with the Secretary of the Association, H. C. Reed, 22 East 16th St., New York, N. Y.

Chemical Equipment Association

On May 10, following the work of the Committee on Organization, financed by twenty-five chemical process equipment manufacturers, the constitution and by-laws of the Chemical Equipment Association were ratified and this new group of manufacturers began work as outlined under the aims and purposes of the Association:

Encourage high standards in the industry.

Promote a better knowledge of conditions controlling the industry's development.

Take steps to bring about definite understanding as to professional services rendered to purchasers in connection with sale of equipment.

Investigate conditions surrounding the resale of equipment originally produced for specific purposes.

Disseminate information as to methods of arriving at correct costs.

Standardize trade phrases.

Collect and disseminate information as to design, raw material and construction.

Take suitable and timely notice of, and action upon, matters of legislation, both national and state, which affect the members of this Association.

Collect and disseminate market statistics, both domestic and foreign.

Collect and disseminate information as to labor conditions and relations.

And enter into such other legitimate Trade Association activities as may be deemed in the interest and welfare of the industry.

It is distinctly understood that this Association will not undertake any activity which will restrain trade, limit production or competition, regulate prices, or otherwise be in violation of the law.

The morning session was addressed by W. A. McCullough, Chairman of the Fabricated Products Division of the United States Chamber of Commerce, and Wm. A. Durgin, Chief of the Division of Simplified Practice of the Department of Commerce. In the evening the purposes of industrial exhibitions, methods of management, finance, and promotion of these exhibits were discussed by Alfred Reeves, Manager of the Automobile Chamber of Commerce, F. W. Payne, Manager of the National Exposition of Chemical Industries, and Roberts Everett, Secretary and Manager of the Association of Ice Cream Supply Men. Each of the speakers presented in informing fashion the details of dissimilar projects, and the resulting discussion brought out many valuable data.

The Organization Committee will function for the Association until the Annual Meeting next September. This Committee consists of George Lehman, *Chairman;* J. C. Kimberly, *Acting Chairman;* A. A. Holmes, *Secretary;* Paul O. Abbé, and P. C. Kingsbury. The committees provided in the constitution will be appointed at once, including a nominating committee and a committee on exhibitions. There are approximately 200 firms, organizations, or individuals who are known to be eligible to active membership, and an active campaign will be undertaken at once.

Those attending the organization meeting were as follows:

Paul O. Abbé, Paul O. Abbé, Inc.
R. C. Campbell, United Filters Corporation
A. N. Bowes, Read Machinery Co.
G. E. Walker, The Dorr Co.
Samuel J. Baril and M. Sultzer, Maurice A. Knight
H. T. Matthews, Quigley Furnace Specialties Co.
R. H. McCready, and Lloyd Lamborn, *Chemical Age*
C. L. Bryden, Vallez Rotary Filter Press and Chemical Equipment Co.
M. W. Smith, Duriron Co.
G. B. Wright, Nash Engineering Co.
Walter E. Lummus, Walter E. Lummus & Co.
A. H. Stevens, Bethlehem Foundry & Machine Co.
L. D. Vorce, Precision Instrument Co.
A. A. Holmes, E. B. Badger & Sons Co.
J. C. Kimberly, Schutte & Koerting
H. C. Parmelee and Irving Fellner, *Chemical and Metallurgical Engineering*
D. L. Dowling, Aterite Company
E. P. Specht, *Oil, Paint and Drug Reporter*
D. H. Killeffer, *Drug and Chemical Markets*
H. E. Howe, *Journal of Industrial and Engineering Chemistry*
F. W. Robinson, E. G. Nellis, and F. M. Turner, Jr., Chemical Catalog Co., Inc.
R. S. Beecher, General Ceramics Co.

Banquet, Meeting of Cleveland Section, A. C. S., Akron, Ohio, May 3, 1922

Meeting in Akron

One type of profitable activity made possible by the American Chemical Society was well illustrated and emphasized by the recent meeting of the Cleveland Section who were guests of the Akron members on May 3. The general region for miles about Akron was represented, and, thanks to careful organization and excellent transportation facilities, about 350 members of the Society availed themselves of the unusual opportunities offered through the coöperation of the B. F. Goodrich, Firestone, and Goodyear Rubber Companies, Maurice A. Knight, the Robinson Clay Products Company, Philadelphia Rubber Works Company, Quaker Oats Company, and the Colonial Salt Company, really to see these various enterprises in active operation. The visitors in groups were guests at luncheon at the three Akron rubber companies named, and in the evening the ball room of the Portage Hotel was filled to its utmost capacity for the dinner and the program.

With Dr. W. C. Geer as toastmaster, the importance of the all-day meeting was emphasized by the attendance of Mayor D. C. Rybolt and J. B. Huber, Past President of the Chamber of Commerce. The fact that executives of the various companies named found themselves able to attend the dinner and hear the talks gave the impression that the importance of industrial chemistry is recognized in Akron. In addition to the industrial excursions during which such unusual courtesies were extended as that by the Quaker Oats Company, which demonstrated that some food is shot from guns, an unusual attraction was the attendance of President Smith, who addressed the dinner in his well-known interesting fashion. He emphasized the service which American chemists have rendered to the nation and to industry and to public welfare ever since 1792. Other speakers were Drs. A. W. Smith and C. L. Parsons, and Mr. H. E. Howe.

Of course meetings of this sort require a great deal of planning and work on the part of a few. All who participated in the activities of the day were convinced that the effort was well worth while, and that the more often Sections can arrange such full days for instruction, get-together, and entertainment, the more will the important activities of Local Sections of the Society be emphasized, particularly to the younger members.

National Research Council Fellowships in Physics and Chemistry

The National Research Fellowships in Physics and Chemistry were established in 1919 under a grant of funds by the Rockefeller Foundation. This grant appropriated $100,000 per year for a definite period of years, and the terms of this grant involved the stipulation that the funds were to be used to stimulate research in the United States in subjects fundamental to physics and chemistry. The administration of the funds was placed in the hands of the National Research Council, which has delegated the supervision of these fellowships to a group of physicists and chemists known as the National Research Fellowship Board.

This Board has adopted no rigid rules of procedure, but has guided itself by endeavoring to select only exceptional students in the fields of mathematics, physics, and chemistry. For the most part, fellowships will be awarded to American citizens who have had training equivalent to that represented by the Doctor's degree; and Fellows are expected, and will be permitted, to conduct their investigations at any American institution that will coöperate in meeting their needs. In those rare cases where facilities in this country are not available for the proper prosecution of a given research, the Board will consider applications for work at properly equipped institutions abroad. Fellows are appointed for one year, but are eligible for reappointment, ordinarily with increase of salary the second year where the original appointment was at the minimum rate of $1800 per year.

An applicant is required to submit with his application for a fellowship the subject and a brief summary of his proposed research, together with one or more institutions—preferably not that at which the major part of his work has been carried on—at which, in his opinion, his work can be conducted to the best advantage.

Research Fellows are expected to devote their entire time to research, except that during the college year they may, at their option, give not more than one-fifth of their time to teaching of educational value to themselves, or to attendance on advanced courses of study. They may associate graduate students with their researches. Fellows are expected to submit to the Board

	Fellows	Location
Atomic and Molecular Structure		
Atomic and Molecular Structure: 1—A Study of the Factors Which Determine the Existence and Intensity of Secondary Valence Unions. 2—A Quantitative Study of the Action of Antagonistic Electrolytes upon Emulsions, Sols, and Jels	George L. Clark	Harvard University
Molecular Models of the Hydrocarbons	Jared K. Morse	University of Chicago
Ballistics		
General Investigation of Movement of Small Rigid Bodies through Fluids, etc.	L. T. E. Thompson	Kalamazoo College
Catalysis		
A Study of the Mechanism of Catalytic Action in the Synthesis of Ammonia	A. F. Benton	California Institute of Technology
The Mechanism of the Catalytic Combination of Ethylene and Hydrogen in Presence of Copper, Especially with Reference to the Radiation Theory of Catalysis and the Influence of Adsorption	Robert N. Pease	Princeton University
Conductivity of Liquids		
A Redetermination of the Absolute Value for the Specific Conductance of Certain Standard Solutions	Henry C. Parker	Clark University
Crystallography		
Correlation of Some Optical and Electrical Properties of Crystals	Joseph Valasek	University of Minnesota
Electricity		
The Behavior of Inductance Coils at High Frequencies, Atomic Theory as Borne Out by Experiments on Photo-electric Effects	Gregory Breit	University of Leyden (Holland)
Electronics		
A Study of the Relations between the Existence of So-called "Free" Electrons in Gases at Low Pressures, the Abnormal Mobility of Negative Ions at These Pressures, and the Mechanism of Ion Formation from Electrons and Neutral Molecules	Leonard B. Loeb	University of Chicago
Study of Position and Properties of Odd Electrons in Molecules Containing an Odd Number	Axel R. Olson	University of California
Positive Ray Analysis Applied to Ionization by Electron Impact	H. DeW. Smyth	Cambridge University (England)
Heat		
Verification of the Third Law of Thermodynamics	F. R. Bichowsky	University of California
Studies in the Thermal Chemistry of Colloids	F. L. Browne	University of Wisconsin
The Specific Heats, Heats of Vaporization, and Vapor Pressures, Measured from Ordinary Temperatures to the Temperatures of Liquid Hydrogen and Liquid Helium, of Methane, Ethane, and Propane, in the Pure State; also of Their Mixtures over as Wide a Range of Temperature and Pressure as Possible	A. G. Loomis	Bureau of Mines
Humidity		
The Measurement of Free-Air Humidities	Geo. P. Paine	Harvard University
Inorganic Chemistry		
The Equations of State of Gaseous and Liquid Argon	Jas. A. Beattie	Massachusetts Institute of Technology
Isotopes		
The Resolution into Isotopes of Mercury and Other Elements (Nickel, Zinc, and Selenium) by a Continuous Method of Multiple-Stage Fractional Diffusion	R. S. Mulliken	University of Chicago
Mechanics of Fluids		
(General) The Importance of Surface Energy as a Factor in Equilibrium (Particular) A Study of Adsorption from Solution or Effect of Surface Curvature on Liquid Solubility	David C. Jones	University of London
Organic Chemistry		
The Ammonia System of Acids, Bases, and Salts	F. W. Bergstrom	Stanford University
The Chemistry of Systems Containing Protein	Edwin J. Cohn	Harvard University
The Colloidal Chemistry of the Hydrous Oxides	Allen Garrison	Rice Institute
The Preparation of Electromers of Benzene Substitution Derivatives	M. C. E. Hanke	University of Chicago
Mild Organic Oxidations	R. N. Harger	Yale University
Mercuri-Organic Derivatives	Morris Kharasch	University of Chicago
The Synthesis of Water-Soluble Derivatives Suitable for Therapeutic Testing. A Continuation of the Reactions of the Arsines	Chas. S. Palmer	University of Illinois
Photochemistry		
The Photochemistry of Visual Purple and Allied Photosensitive Systems	Selig Hecht	Harvard University
The Minimum Amount of Energy of Monochromatic Light Required to Blacken a Grain of Silver in a Photographic Plate	P. S. Helmick	Princeton University
Physiological Physics		
Sensitivity of Normal and Abnormal Ears for Tones of Various Frequencies	John P. Minton	University of Chicago
Spectroscopy		
The Fine Structure of the Infrared Absorption Bands of Gases	E. F. Barker	University of Michigan
The Relative Intensities of the Components of Some Lines as Found in the Stark Effect for Helium	J. S. Foster	Yale University
The Spectroscopy of the Rare Earths: Studies in the Ultraviolet Spectra	L. F. Yntema	Yale University
X-Rays		
Factors Influencing the Intensity of Reflection of X-Rays from Crystals	R. G. Dickinson	California Institute of Technology

shortly before March 1 of each year a detailed report on the progress of their researches, and must present an account of their researches in form for publication before withdrawing from the fellowship. It is understood that all results of investigations by the Fellows shall be made available to the public without restriction. Fellowship appointments are subject to the condition that after they are accepted by the applicant, they will not be vacated within the year without consent of the Research Fellowship Board.

Applications for these fellowships should be made on the form provided for that purpose, and should be sent to the Secretary of the Research Fellowship Board, 1701 Massachusetts Ave., Washington, D. C., to whom all other correspondence should also be addressed.

The personnel of the Fellowship Board consists of:

SIMON FLEXNER, *Chairman*, Director of Laboratories, Rockefeller Institute for Medical Research.

HENRY G. GALE, Executive Secretary, Professor of Physics, University of Chicago, Chairman of the Division of Physical Sciences, National Research Council.

F. G. COTTRELL, Chairman of the Division of Chemistry and Chemical Technology, National Research Council.

GEORGE E. HALE, Director of Mount Wilson Observatory.

JOHN JOHNSTON, Sterling Professor of Chemistry, Yale University.

ELMER P. KOHLER, Professor of Chemistry, Harvard University.

ROBERT A. MILLIKAN, Director of the Norman Bridge Physical Laboratory, California Institute of Technology.

AUGUSTUS TROWBRIDGE, Professor of Physics, Princeton University.

The present National Research Fellows are grouped under their various fields of research, with their specific problem and location, indicated on page 566.

The following group comprises the fellowships granted by the Board which have expired:

Thermoelectricity and Metallic Conduction	A. E. Caswell	Princeton University
Measurement of the Intensity of Reflected X-Rays	R. A. Patterson	Harvard University
Effect of Magnetization of Iron on Its Absorption of Monochromatic X-Rays and Γ-Rays	A. H. Compton	University of Cambridge (England)
Catalysis in Homogeneous Systems with Special Reference to the Catalytic Activity of the Hydrogen Ion in the Hydrolysis of Sucrose	Warren C. Vosburgh	Columbia University
Study of Specific Heats and Other Properties of Substances at Low Temperatures	W. H. Rodebush	University of California
A Study of the Adsorption of Vapors on Glass and Quartz at Various Pressures and Temperatures	E. K. Carver	Harvard University

W. E. TISDALE

NATIONAL RESEARCH COUNCIL
WASHINGTON, D. C.

Society of Industrial and Micrographic Photography

On May 10, the Society of Industrial and Micrographic Photography was organized at the Chemists' Club in New York. The importance of photography in industry is not realized by most people, and it is the purpose of the Society to emphasize the importance of the art and to assist in its development. A further meeting to discuss and ratify the constitution and by-laws will be held June 14 at the Chemists' Club. In the interim the following serve as an executive committee charged with preparing the constitution:

President: JAMES MCDOWELL, Sharp and Hamilton Manufacturing Co., Boston.

Secretary and Treasurer: THOMAS J. KEENAN, Editor of *Paper*, New York.

Vice Presidents: J. H. GRAFF, Brown Company, Berlin, N. H.; BENNETT GROTTA, Atlas Powder Co.

Petroleum Section, A. C. S.

The Petroleum Section of the A. C. S., in its campaign for the promotion of research on petroleum chemistry, desires the coöperation of every person interested, and therefore requests that all members interested in petroleum chemistry and technology write their names, addresses, and business connections on postcards and forward them to W. A. Gruse, *Secretary*, Mellon Institute, Pittsburgh, Pa.

Meeting of the American Electrochemical Society, Baltimore, April 27, 28, and 29, 1922

The 41st General Meeting of the American Electrochemical Society at Baltimore was one of the most interesting and attractive in the history of the Society. The attendance was beyond all expectations and the program covered every variety of taste.

ELECTRIC CAST IRON

The outstanding feature of the technical program was the Symposium on Electric Cast Iron in which about thirty members participated. Mr. George K. Elliott of the Lunkenheimer Company outlined some of the more important problems bearing on the production of cast iron in the electric furnace. The cold charge process for cast iron probably never will acquire more than a scattered application, and the greatest possibilities seem to lie with the duplexing process. This process apportions refining to the electric furnace, and therefore the most logical hearth for the electric furnace is the most potently refining one, in other words, the basic hearth. The electric furnace is at its best when coupled with a chemical laboratory in an intimate manner. By sampling the molten iron as soon as transferred from the cupola the laboratory can determine as many elements as desired, and the proper additions can be made before the metal is ready to pour, making possible the closest regulation of the composition. The most striking reaction taking place in the basic electric furnace is desulfurization. Mr. Elliott discussed this phase in detail and also dwelt upon the deoxidation problem. W. E. Moore of Pittsburgh outlined the History of Electric Cast-Iron Melting. It is only since 1914 that the process is in regular operation. Mr. Moore believes that there is an even broader field for the electric iron furnace than for the increasingly popular electric steel furnace. Jas. L. Cawthon, Jr., of Pittsburgh, commented at length on the individual elements C, Si, Mn, S, and P entering into the composition of "Synthetic Cast Iron." The basic process provides facilities for reducing S and P, while the acid process is lower in cost and simpler in operation and the slag is much easier to handle in casting from lip pour ladles or shanks. Robert Turnbull of the U. S. Ferro Alloys Corporation pointed out that both open top smelting type furnaces and steel furnaces have been used in the manufacture of synthetic iron. The open top type is easier to operate and permits a higher carbon to be obtained in the finished iron than with the steel furnace. The smelting of iron ore electrically is a problem that will eventually have to be met, as a day will come when coke will be no longer available, and as it becomes scarcer, an ever-increasing cost in this commodity can be expected. Dr. Richard Moldenke related in detail the new developments in Germany where he has recently visited important steel and iron mills. Duplexing of cast iron is carried out at a number of mills and foundries. Messrs. Clyde E. Williams and C. E. Sims of the Bureau of Mines, Seattle Station, reported upon their results on the "Study of Carburization in the Manufacture of Synthetic Cast Iron." Graphite, because of its lower ash and higher density, has given slightly better results than any of the other forms of carbon. Sulfur probably decreases the rate and the degree of carburization. Phosphorus has no effect upon the rate or the degree of carburization; similarly, silicon has no effect. Manganese seems to increase both the rate and the degree of carburization. Messrs. H. M. Williams and T. B. Terry of the General Motors Research Corporation are "Melting Cast Iron in the Booth Rotating Electric Furnace." They find that this popular brass melting furnace is adaptable to all types of cast-iron melting where refining by slagging is not required.

W. E. Cahill of the Alaska Treadwell Gold Mining Co. submitted figures to show that in Treadwell cast iron is made more cheaply in the electric furnace than in the cupola. The removal of S is not dependent upon carbon in the steel, but upon the length of time the steel is held under a carbide slag. R. C. Gosrow of Buffalo compared the "Shaft and Open Top Furnaces in the Manufacture of Pig Iron Electrically from Iron Ore." Mr. Gosrow believes that with large units of 7000- to 10,000-kw. capacity, the open top furnace will be the practical unit. Messrs. Lyman C. Judson and Harry P. Martin of Niagara Falls gave a brief summary of all publications on the "Electric Furnace in the Iron Foundry" that have appeared within recent years.

The symposium was most ably conducted by Acheson Smith, A. T. Hinckley, and Bradley Stoughton who alternated in presiding. Frank Hodson of Philadelphia suggested that the Electrothermic Division, under whose auspices the symposium had been held, prepare a small pamphlet embodying the many valuable points brought out. The discussion lasted all of Thursday morning and afternoon. At dinner the Electrothermic Council met to discuss future plans.

OTHER MEETINGS

Thursday evening the members were invited to a lecture by Professor R. W. Wood of Johns Hopkins on "Fluorescence." Professor Wood performed some very striking experiments and commented upon his work during the war in detecting hidden messages in passports and the development of his special green glass, transparent to ultraviolet rays but opaque to the visible rays.

Friday morning was devoted to reading of papers on electrolytic subjects by W. C. Moore, W. B. Jones, E. F. Kern, M. Y. Chang, R. J. McKay, Helen C. Gillette Weir, O. W. Brown, J. C. Warner, W. G. Allan, and E. R. Weaver. In opening the session President Smith presented an address on "The Technical Man as Citizen," emphasizing the grave need for the chemist and metallurgist to participate actively in the affairs of the state.

For Friday afternoon the Steamer Latrobe had been chartered and the members enjoyed a cruise on the bay. Two stops were made, one at the U. S. Industrial Alcohol Plant and the other at the Davison Chemical Company's plant. At the latter a very instructive demonstration on the applications of Patrick's silica gel was included.

The Smoker, one of the "snappiest" ever arranged for, was scheduled for Friday evening. Mr. F. M. Boyles and his associates on the committee know how to entertain. One of the climaxes during the course of the evening was the award of the Gerkin & Pickles medal to H. C. Parmelee. The local committee spared no effort in making the visit of the electrochemists as enjoyable and interesting as possible.

Saturday morning was devoted to the reading and discussion of papers on electrodeposition and miscellaneous subjects. The authors who contributed were Victor F. Hess, Carl Hering, Duncan MacRae, W. E. Hughes, M. R. Thompson, W. G. Horsch, T. Fuwa, and U. C. Tainton. The discussions were unusually animated and prolonged.

Dr. Carl Hering was elected to Honorary Membership in the Society. He has been a most ardent and enthusiastic member of the Society from the very start and his scholarly contributions have gained for him a world-wide reputation. The new officers of the Society are: Dr. C. G. Schluederberg, *President;* H. C. Parmelee, A. H. Hooker, and W. S. Landis, *Vice Presidents;* A. T. Hinckley, W. M. Corse, and Wm. Blum, *Managers;* F. A. Lidbury, *Treasurer;* and Colin G. Fink, 101 Park Ave., New York, *Secretary*. The fall meeting will be held in Montreal, September 21 to 23, 1922. Two of the main subjects scheduled for this meeting are "Industrial Heating" and "Electro-osmosis."

COLIN G. FINK, *Secretary*

NEW YORK, N. Y.

Willard Gibbs Medal

The Willard Gibbs Medal will not be awarded this year.

Calendar of Meetings

American Oil Chemists' Society—13th Annual Meeting, New Orleans, La., June 5 and 6, 1922.

Institute of Metals Division of A. I. M. E.—Rochester, N. Y., June 5 to 9, 1922.

National Fertilizer Association—29th Annual Convention, White Sulphur Springs, W. Va., week of June 12, 1922.

National Lime Association—Annual Convention, Cleveland, Ohio, June 14 to 16, 1922.

American Institute of Chemical Engineers—14th Semiannual Meeting, Niagara Falls, Ontario, June 19 to 22, 1922.

American Leather Chemists Association—19th Annual Meeting, Ontario, Canada, June 21 to 23, 1922.

Alpha Chi Sigma Fraternity—7th Biennial Conclave, St. Louis, Mo., June 22 to 24, 1922.

American Association for the Advancement of Science—Joint Meeting with Pacific Division of the Association, Salt Lake City, Utah, June 22 to 24, 1922.

American Society for Testing Materials—25th Annual Meeting, Atlantic City, N. J., June 25 to July 1, 1922.

American Chemical Society—64th Meeting, Pittsburgh, Pa., September 5 to 9, 1922.

Eighth National Exposition of Chemical Industries—New York, N. Y., September 11 to 16, 1922.

Commercial Engineering Conference

The second public Conference on Commercial Engineering was held at Carnegie Institute of Technology, Pittsburgh, Pa., on May first and second, under the direction of the Committee on Commercial Engineering of the United States Bureau of Education.

At the opening session, the discussion dealt with "Current Practices in Colleges and Universities Relating to Business Training for Engineers and Engineering Training for Business Men." The second session discussed "Coördination of College Training with the Industrial Demand," and the third treated "Civic and Social Training of the Engineer and Business Man." The final session was devoted to group conferences on the same subjects.

The most striking thing about the Conference was the active interest of large men of affairs from the outside world. The discussions became so energetic that every meeting went far past its scheduled time. The Conference undoubtedly brought about a feeling of closer coöperation between outside men and the educators.

The spirit of the Conference was that the technical man must have an appreciation of business, and the business man of technical matters; and the educator should know enough of both properly to prepare his students for the outside world.

American Institute of Chemical Engineers

The 14th Semiannual Meeting of the American Institute of Chemical Engineers opens at Hotel Clifton, Niagara Falls, Ontario, on Monday, June 19, 1922.

The first day's program includes papers on the concentration of sulfuric acid and nitric acid solutions. Tuesday, June 20, will be devoted to a trip to Toronto by boat from Lewiston. On Wednesday, the meetings will be transferred to Hotel Lafayette, Buffalo, N. Y. They will deal with the manufacture of nitric acid, the manufacture of hydrogen and nitrogen for synthetic ammonia manufacture, and hydrochloric acid manufacture. The afternoon will be devoted to visits to manufacturing plants in Buffalo. The last day of the meeting, Thursday, June 22, will be spent in Niagara Falls, Ontario, again. Papers will treat of the production of hydrochloric acid and of phosphoric acid.

Industrial Division—Pittsburgh Meeting

The Pittsburgh Meeting begins September the fourth and ends on the ninth. There are already many indications that this meeting will be one of the best ever held by the SOCIETY.

Members who are planning to present papers before the Industrial and Engineering Division should prepare abstracts at the earliest possible moment and send them to the Secretary. It is our aim to send out copies of the abstracts to the members so that they may know some time in advance of the meeting something of the nature of the papers to be presented and thus be in a better position to take part in the discussion.

There will be a symposium upon Automatic Process Control. Here papers dealing with the fundamentals underlying the different practical methods of automatic process control will be given. Industrial and university workers have been asked to prepare papers for this feature of the Division's program. Such a symposium cannot help but be of vital importance to industrial men.

The coming of summer with its long-looked-for vacation periods necessitates the early preparation of the paper and abstract for the Pittsburgh Meeting.

ERLE M. BILLINGS, *Secretary*

EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

The following have been appointed as the official delegates of the United States to the International Chemical Conference at Lyons: C. L. Parsons, *Chairman;* E. W. Washburn, *Vice Chairman and Secretary,* R. B. Moore; H. S. Washington; Edward S. Chapin; and Edward Bartow.

NOTES AND CORRESPONDENCE

Calculation of Vapor Pressures of Naphthalene, Anthracene, Phenanthrene, and Anthraquinone by Dühring's Relation

Editor of the Journal of Industrial and Engineering Chemistry:

There appeared in a recent issue of THIS JOURNAL an article entitled "Vapor Pressure Determinations on Naphthalene, Anthracene, Phenanthrene and Anthraquinone between Their Melting and Boiling Points,"[1] which offers some new and valuable data. It may be worth while to point out in this connection that such data for a great variety of materials can be calculated with reasonable accuracy provided only two points on the vapor pressure curve are known. This is not intended to detract in the slightest from the article referred to, but to bring to the attention of industrial chemists and engineers the usefulness of a simple vapor pressure relation empirically discovered by Dühring.[2] The calculated results will of course not be as accurate as the experimentally determined ones, but are sufficiently accurate for all engineering design and for 95 per cent of the cases in which industrial chemists would make use of them.

This relation may be expressed in a simple mathematical way as follows:

$$t'_A - t_A = K\,(t'_B - t_B)$$

where t'_A = any temperature of the substance in question.
t'_B = temperature at which a reference substance has the same vapor pressure as the substance in question has at t'_A.
t_A and t_B = any other temperatures at which the two substances have the same vapor pressure.

In other words, t'_A and t'_B and t_A and t_B are "corresponding" boiling points; that is, the boiling point of substance A and substance B, respectively, under the same pressure. From the form of the equation it is at once apparent that there is a linear relation between t'_A and t'_B. Consequently, the simplest way to use this relation in the estimation of vapor pressures is by means of a plot of t'_A *vs.* t'_B. In general the substance chosen as a standard should be somewhat related to the substance whose vapor pressure is to be determined, but in a great majority of cases water is satisfactory and by far the most convenient because vapor pressure tables of water are readily available. Since the relation is linear, only two points are needed to determine the whole curve, and one of these points may be determined by the normal boiling points of the substance and water. The rule for using this relation may then be stated as follows: On a plot of temperature of substance *vs.* temperature of water, locate the point corresponding to the normal boiling points and one other point at which the two have the same vapor pressure. Draw a straight line between these two points. From this straight line read off the temperature of water corresponding to the temperature at which the vapor pressure of the substance is desired. The vapor pressure of water at this temperature taken from a table is then the desired vapor pressure of the substance.

The accompanying plot was made in this way for the four substances shown. The normal boiling points were chosen for one point in each case and the lowest temperatures at which the vapor pressures were determined in the article referred to, were chosen for the other points. Consequently, with a knowledge of one vapor pressure for each substance in the neighborhood of 10 to 100 mm. and the other at 760 mm., we can interpolate for all vapor pressures between or, if desired, extrapolate beyond these limits. Referring to the plot, the outside points indicated on each curve are the chosen ones and the indicated points between are observed points. To illustrate more clearly the use of the relation, consider Curve I, for anthraquinone. If the vapor pressure at 320° C. is desired, find the point on the scale of abscissas corresponding to 320° on the scale of ordinates for Curve I. This is about 69.8° C. Looking up the vapor pressure of water at 69.8° C., we find it to be 231.3 mm., which

TABLE I

	ANTHRAQUINONE			PHENANTHRENE	
TEMP. ° C.	Calculated Vapor Pressure Mm.	Observed Vapor Pressure Mm.	TEMP. ° C.	Calculated Vapor Pressure Mm.	Observed Vapor Pressure Mm.
300	148.2	147.8	240	77.1	79.0
310	186.6	186.0	260	130.5	135.5
320	231.3	232.0	280	213.8	220.0
340	354.9	354.5	300	335.2	343.7
360	527.5	531.7	320	511.7	518.8
370	636.0	643.4	330	624.4	629.4
	ANTHRACENE			NAPHTHALENE	
240	76.3	76.0	100	19.9	18.5
260	128.1	129.1	120	43.0	42 7
280	208.2	211.0	140	86.2	88.7
300	327.1	332 0	160	163.3	168.4
320	496.2	502.9	180	291.2	299.1
			200	494.3	502.1
			210	631.3	937.2

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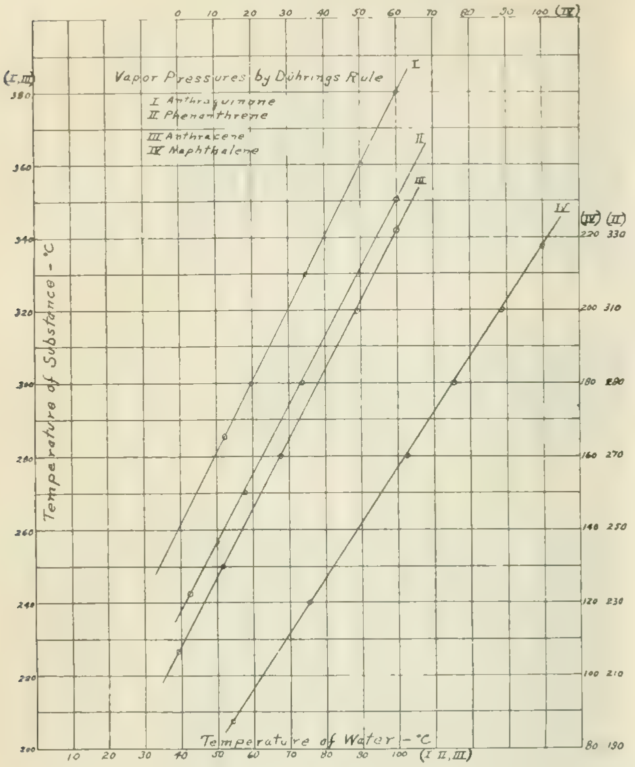
[1] Nelson and Senseman, THIS JOURNAL, **14** (1922), 58.

[2] "Neue Grundgesetze der rationellen physik und chemie," Leipzig, **1878**.

is the desired vapor pressure of anthraquinone at 320° C. The value experimentally determined is 232.0 mm.

In Table I the vapor pressures determined from Dühring's relation (by means of a large-scale plot) are compared with the observed values of Nelson and Senseman.



To realize that these are very good checks, it is necessary only to refer to Landolt-Börnstein and note the disagreement between vapor pressure determinations on the same substance by different observers. Even better agreement can be obtained by choosing, instead of two extreme points over the range desired, one point about the middle of the range and the normal boiling point as the other.

There are, of course, other vapor pressure relations, one of the best of which is the Ramsay-Young equation.[3] This is expressed mathematically as follows:

$$\frac{T'_A}{T'_B} = \frac{T_A}{T_B} + C(T'_A - T_A)$$

where, as in Dühring's equation, T'_A and T'_B are the boiling points of two substances under one and the same pressure and T_A and T_B are boiling points of the same substances under another pressure (the same for both), and C is a constant to be evaluated from known values of the boiling points. The temperatures are on the absolute scale, though it is very probable that a similar relation would hold for centigrade temperatures. As with Dühring's relation, the constant may be evaluated when the boiling points of A and B are known at only two pressures, one of which is conveniently chosen as 760 mm. Calling the ratio $\frac{T_A}{T_B} = R$, we may transform the equation to:

$$T_A = \frac{T'_B\,(R - CT_A)}{1 - CT'_B}$$

Then by assigning any values we choose to T'_B, we may calculate the boiling point T'_A of the reference substance just as with Dühring's relation.

There are, however, one or two very important differences between the two equations from a practical standpoint. Dühring's equation is a linear one, whereas the Ramsay-Young equation is of the second degree. This difference is not appreciable if one wishes merely to calculate the vapor pressure of a substance at one or two temperatures, but if one wishes to obtain vapor pressures over a range of temperatures, Dühring's equation is much the simpler to use. As shown above, by Dühring's relation the whole vapor pressure curve over a wide range can be located in a few moments merely by locating two points and drawing a straight line between them. With the Ramsay-Young equation it would be necessary to calculate a number of points and plot them. Furthermore, Dühring's relation can be stated as a rule in a very simple way which is easy to remember, so that one can make use of it without having to refer to a textbook to determine the form of the equation.

On the other hand, the Ramsay-Young equation is more accurate than Dühring's equation. This is shown by Table II, which compares the vapor pressures of phenanthrene calculated by the two equations.

TABLE II

Temp. °C.	Vapor Pressure Observed Mm.	by Ramsay-Young Equation Mm.	by Dühring Equation Mm.
240	79.0	77.5	77.1
260	135.5	132.5	130.5
280	220.0	216.6	213.8
300	343.7	339.4	335.2
320	518.8	515.6	511.7
330	629.4	627.8	624.4

In general, the difference in accuracy is not great enough to warrant the use of the more complicated equation, especially when one remembers that the accuracy of the results also depends on the accuracy with which the vapor pressures at the two chosen points are known.

BARNETT F. DODGE

HARVARD UNIVERSITY
CAMBRIDGE, MASS.
February 25, 1922

Selling the Industry to the Chemists

Editor of the Journal of Industrial and Engineering Chemistry:

An industrial editor has a splendid opportunity to be of unusual service to chemists, especially of the younger generation, by selling the industry to the chemist rather than chemistry to the industry.

Too many graduates in chemistry leave school to-day with a fatal misconception of the mental state of industrial leaders. They get to look upon industries such as ours as living in the dark ages and developing by rule-of-thumb or haphazard methods, while, with their training in chemistry, they hold a sort of Aladdin's lamp capable of revolutionizing the industry. Allowing such a false notion to grip the mind of a student is probably one of the worst crimes of modern systems of education, for the result, so far as the student's career is concerned, is often fatal.

The great success of a certain class of tanners, for example, has been due to the development of a science of leather manufacture, as distinct from the art, based upon a belief in the constancy of natural laws and involving the organization and classification of countless facts gained by experience or handed down from previous generations. This science, because of its high degree of specialization, has proved more powerful in a practical way than chemistry, so much so that chemistry must still be regarded as of value primarily in supplementing and not replacing the science of the tanner. Disillusionment has been common among chemists entering this industry, as the result of the unexpected intricacy of the application of chemistry to leather manufacture, of insufficient training, of false notions of superiority over artisans who had devoted their lives to the industry, or of failure to appreciate that the tanner's own science is usually far more reliable than the chemistry of a beginner in the industry.

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[3] *Phil. Mag.*, [5] **20** (1885), 515; **21** (1885), 33; **22** (1886), 37.

After his first glimpse of the tannery, the chemist is apt to look upon the tanner as an old fogey. After the first dozen attempts at improving the processes through chemistry, the chemist usually looks to the tanner like an amateur fourflusher. At this juncture, the chemist often gets relegated to a cubby hole where he can do no harm to the process or is elected to the "once-worked-heres."

In order to make substantial progress, the chemist must, as a rule, devote himself completely to a study and explanation of the mechanism of each step of a successful process, without in any way interfering with the process. Once available, sound explanations of the mechanism of existing processes are of incalculable value in suggesting practical experiments leading to the elimination of unnecessary operations and to the improvement and development of others. That this procedure has not been more widely adopted is easily explained. Long and costly studies are required for which there is no immediate return, and whether there will ever be a return commensurate with the cost of the studies must depend upon the skill of the chemist, which it is difficult for the tanner to judge. Moreover, the qualifications required of the chemist are extremely severe. He must have a broad, theoretical training, marked ability to advance the pure science, and great skill in adapting delicate apparatus to crude, tannery conditions. On the other hand, previous contact with the industry is quite unnecessary.

I presume this must be true for most complex industries. What is the use of trying to sell chemistry to industry unless employer and chemist understand each other, and that their task is purely a coöperative one and hopeless unless the chemist is a real chemist of a high order? When the university and industry really begin to understand each other's needs, potentialities, and limits, they are bound to coöperate more extensively and to their mutual benefit. The readers of our Journals are chemists, and the task of an industrial editor would therefore be to present the industry in its true light to the chemists who do not have an intimate contact with industry and are not aware that many successful industrial men, though less well known, are on a mental par with many of our great scientific leaders.

JOHN ARTHUR WILSON

203 JUNEAU AVE.
MILWAUKEE, WIS.
April 3, 1922

American-Made Glassware

Editor of the Journal of Industrial and Engineering Chemistry:

The editorial "Our Viewpoint," in the March issue of THIS JOURNAL, leads me to believe that our experience at Grove City College may be of interest in the case for American-made apparatus.

Last year we supplied four Pyrex beakers to each of ten students in a course in quantitative analysis which ran twenty-four weeks. At the end of about 150 hours of laboratory work per student, thirty-nine beakers were returned to the stockroom. In previous years even with Jena glass, two to five beakers were broken by each student in the same course. The breaking of *one* beaker instead of a minimum of *twenty* is a striking argument for American glass. Our experience with other articles and with American porcelain in this and other courses is equally as favorable.

The original investment per student will be somewhat higher when he is furnished with American supplies than when he is furnished with imported glass and porcelain. The cost of upkeep of stock and the breakage per student is certainly much lower. The lower breakage results in better work done in shorter time, as the loss of experiments due to broken apparatus is much less.

As to more special apparatus, the shorter time for delivery is important. Repairs or replacement of parts can be made more quickly in case of American apparatus, while repair of foreign apparatus is frequently impossible or, at least, extremely slow. If apparatus is bought with a view to continuity and dependability of service and not to fill museum shelves, the thoughtful, careful buyer must invariably decide in favor of the American product.

Yours for American supplies because of dependability and lower ultimate or net cost, to say nothing of the patriotic pride in articles of the very highest grade.

O. J. SIEPLEIN

GROVE CITY COLLEGE
GROVE CITY, PA.
April 7, 1922

The Value of Graduate Training

Editor of the Journal of Industrial and Engineering Chemistry:

Yesterday I had occasion to go over the records of the students who have received graduate degrees from the department of Chemical Engineering at Columbia. Part of these men have received the degree of Chemical Engineer, and part Doctor of Philosophy, each representing on an average three years of graduate work. The total number approximates 100.

At present there are two of these men who do not have positions. One is traveling in Europe and the other, a man of the class of 1920, has received several offers but insists on staying in New York and has declined to consider openings away from here. He has been out of work for several months. Of course, a number of men have lost their positions and been out of work during this depression, but in each case they have later found positions along their line.

This is, in my mind, an excellent example of the value of advanced training in the field of applied chemistry. There are hundreds of men who have had only collegiate training who lack positions, but the men who have had graduate training are apparently held onto and sought by the industries. The industrial chemical field of the present and the future is in the hands of the man who has had graduate training in addition to college training.

RALPH H. MCKEE

COLUMBIA UNIVERSITY
NEW YORK, N. Y.
March 31, 1922

Heat Transfer. I—Condensing Vapors

Editor of the Journal of Industrial and Engineering Chemistry:

Inquiry has been made as to the details concerning the method of using base metal thermocouples in the determining temperature of metal tubing. [*See* THIS JOURNAL, **14** (1922), 13.]

Two wires of dissimilar metals were treated with borax flux on the tips and fused together for a very short distance, possibly $^1/_8$ in. The thermocouple so formed was polished until bright, inserted in a narrow groove about $^3/_8$ in. long in the outer surface of the metal tube, and soldered flush.

The couples were calibrated in place by filling the apparatus with warm water at the same temperature on both sides of the tube.

The couple obviously indicates the temperature of the outer surface of the tube.

W. H. MCADAMS
T. H. FROST

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
April 15, 1922

Wool Scouring Wastes for Fertilizer Purposes

(Correction)

In my article under the above title [THIS JOURNAL, **14** (1922), 434] attention is called to the following error:

2nd col., 2nd para., 4th line, reading "degreased waste contains 24.5 per cent K_2O, 24.5 per cent nitrogen, etc.," should be corrected to read "degreased waste contains 24.5 per cent K_2O, *2.5* per cent nitrogen."

F. P. VEITCH

WASHINGTON, D. C.
May 4, 1922

Report of Committee on Occupational Diseases in the Chemical Trades

(Correction)

In the Report on page 456 of the May issue of THIS JOURNAL

2nd para., lines 2 and 3, delete "and industries;" 6th para., line 5, for "trained" read "engaged."

LEWIS W. FETZER, *Chairman*

UNIVERSITY OF DALLAS
DALLAS, TEXAS
May 9, 1922

LONDON LETTER

By HUGH GRIFFITHS, 15 New Bridge St., London, E. C. 4, England

KEY INDUSTRIES BILL

As was expected, the interpretation of the Key Industries Bill is giving rise to discussion. Various appeals have been heard, the most interesting being that in connection with cream of tartar, tartaric acid, and citric acid. The decision turned on the interpretation of the expression "fine chemical" and the Referee in giving his decision that these substances could not be considered as fine chemicals, and should therefore be excluded from the Act, stated that he had found that there is no commonly accepted definition of a fine chemical, and he could only be guided by trade usage. Lactose "R" has also been excluded from the list.

A most interesting application was made by the agents of an American firm, to have mucic acid removed from the list, mention being made of a new process for producing this substance in large quantities as a substitute for cream of tartar. This appeal was dismissed on the ground that mucic acid had to be considered as a fine chemical at the date of passing the Act.

Applications have also been made to have calcium carbide and liquid sulfur dioxide included in the list. These applications were also dismissed, although a mass of evidence was collected and given by eminent scientists in support of the former application. At the time of writing, synthetic camphor and pinene are under consideration, an application having been made to have these removed from the list. In spite of the elaborate provisions of this Act, there is but little sign of revival in the chemical trade, and there is an increasing tendency to avoid new developments of any kind.

SYNTHETIC AMMONIA

Of all the developments in chemical industry which must be considered as of national importance, those concerning the fixation of atmospheric nitrogen are the most essential. It is somewhat disturbing, therefore, to hear rumors that none of the schemes for the manufacture of synthetic ammonia are really being pushed forward. There is a very persistent rumor that all constructional work on these plants has been stopped. If this rumor be true, the sympathy of every technical man will be extended to those who have done so much to the development of these processes in this country. It is generally felt that money which is being found and spent in other directions might well be devoted to this work, and it is hoped that government support will be forthcoming.

SODIUM SILICATE

In the March letter, a reference was made to a new method of manufacturing sodium silicate. There are several methods having the same object. The object of these methods is to convert the difficultly soluble fusion mass into a form of solid sodium silicate which can be dissolved readily without the use of large quantities of water, and without the use of pressure vessels. Most of these methods are the subjects of patents. Not only do these methods serve entirely to cut out the evaporation process, but they yield solid silicates, both of neutral and alkaline constitution, which can be transported in the solid form and dissolved by the user as required; the saving in transport charges being considerable.

EVAPORATING PLANTS

Considerable interest is being shown in the various evaporating plants which operate on the principle of the reversed heat engine. This principle as applied to technical evaporation is by no means new, and suggested methods date back almost as far as the multiple effect plant. There are now on the market plants according to several different systems, and an English company has been established to handle one type of installation, *i. e.*, the Prache and Bouillon system.

Up to the present the number of these plants in use in this country is not very large, but an evaporator according to this system, of considerable size, is in use in a glue works in the north of England, and certain power stations are installing water distilling plants at the present time according to the same principle.

The deluge of patent applications from abroad relating to "thermo-compression" is very significant, and, coupled with the fact that the makers of these plants will now give satisfactory guarantees as to steam or energy consumption, these plants have to be considered as definite competitors against the multiple effect apparatus.

Some firms will guarantee the same steam economy in a single vessel working at ordinary atmospheric pressure as can be obtained with a triple effect; there should therefore be some prospect that recompression evaporators will be able to enter the field at very competitive prices, but at the present time they are somewhat expensive, and, for the same performance, higher in price than multiple effect plants.

NEUTRAL SULFATE OF AMMONIA

The manufacture of sulfate of ammonia is at last being definitely subjected to radical changes. Manufacturers have gone considerably out of their way to educate the consumer against the ordinary quality of sulfate. It is definitely recognized that a neutral sulfate in a sandy dry form would possess many advantages in practical use, and the consumers are now beginning to show interest and are looking for this material instead of the ordinary quality. The inevitable discussion has arisen as to the best method of manufacturing this neutral sulfate, and numerous patents have been taken out to protect modifications in the processes, neutralization by ammonia gas, ammoniacal liquor, or alkaline salts being proposed and effected in many different ways.

It is apparent, however, that the manufacturers are not quite so pleased with themselves now that they have to produce this material commercially, particularly as most of them find it necessary to instal new plant.

Most of the troubles manufacturers have had seem to be due to their reluctance to spend money on new plant at a time when business is not bright.

There does not appear to be the slightest technical difficulty in making neutral sulfate of ammonia, and it is generally expected that in course of time all sulfate will be delivered in the neutral form, and the time will come when the consumer who will purchase the ordinary quality of sulfate will be forgotten.

April 13, 1922

WASHINGTON NOTES

TARIFF

The opening gun, so far as the chemical world is concerned, was fired on May 2, when the first vote on the chemical schedule of the Tariff Bill was taken. Senate leaders are making every effort to keep the tariff before the Senate for a maximum number of hours each day, and in order to accomplish this the Senate is meeting an hour earlier and is holding night sessions. Senator King is continuing the vitriolic attacks on the dye and chemical schedule which he made before the Shortridge subcommittee.

DYE INVESTIGATION

The hearings which were begun on February 20 by the Senate subcommittee appointed to investigate the dye industry were officially closed on May 16. The subcommittee is at work on its report, which will probably be in the hands of the full committee before THIS JOURNAL issues. It is confidentially believed that the report will state that the dye and chemical industries have proved conclusively that no monopoly exists and that the report will further recommend that these industries be given an unusual degree of protection.

PATENT CONVENTION

The patent convention with Germany has been revived, effective May 8. This action was taken by Secretary Hughes with the understanding that if legislation such as is outlined in the Stanley Bill now pending before Congress is enacted, the revived treaty can be denounced and modification obtained.

The Senate Committee on Patents has also conducted hearings relative to the compulsory working of patents. Such violent opposition to the Stanley Bill has developed that a substitute measure has been proposed which provides that two years after the issuance of any patent, if it be shown that the invention is being worked in a foreign country, the United States Court of Appeals may issue a license making it possible to manufacture under the patent. The substitute measure has the approval of Senator Stanley.

MUSCLE SHOALS

The subcommittee of the House Committee on Military Affairs has submitted its report to the full committee. The outstanding features of the report are that all of the offers should include a definite contract for the manufacture and sale of fertilizer, the exact quantity to be specified, and that no offer should be considered which does not include the entire property.

The Senate Committee on Agriculture is continuing its hearings. Senator Norris, chairman of this committee, is very strongly of the opinion that the Government should handle this stupendous project itself and that none of the offers submitted should be accepted.

PUBLICATION RESUMED

Under the authorization contained in the Senate Joint Resolution No. 132, signed by the President on May 11, the publication of the *Journal of Agricultural Research* will be resumed, beginning with Vol. 22, No. 10, to be dated December 23, 1921. All manuscripts which were previously accepted for publication but which were returned to the authors when publication was discontinued, will be printed if resubmitted.

AGRICULTURAL APPROPRIATIONS

The Agricultural Appropriation Bill, as signed by the President on May 11, provides that during the fiscal year 1923, not more than three scientific investigators or other employees may be paid up to $6500 per annum, that eight may be paid up to $5500 per annum and that the general maximum for others shall be $5000 per annum. The present maximum salary that may be paid from any lump fund appropriation is $4500.

The Bureau of Chemistry receives an increase of $5000 for the purpose of conducting experimental work on cassina, and an increase of $5000 to extend its investigations on cane sirup.

CREATION OF DIVISION OF WAR MINERALS SUPPLY

Effective May 1, a Division of War Minerals Supply was established in the Bureau of Mines. The new division has charge of matters relating to the supply of strategic minerals involved in war plans of the Government, the maintenance of a proper balance of trade among the mineral industries of the nation, and such related duties as may from time to time be assigned to it. H. S. Mulliken, who has for some time acted as special assistant to the Director of the Bureau, has been given charge of the work of this division. The new division will, in coöperation with the Bureau of Foreign and Domestic Commerce, represent the Government in price studies of the nonferrous metals. Its work will be reflected in the weekly quotations published by the *Engineering and Mining Journal-Press* of New York, and will, for the present, relate particularly to the metals of major importance.

FOOD STANDARDS COMMITTEE

The twenty-second meeting of the Joint Committee on Definitions and Standards will be held in the Bureau of Chemistry, June 19 to 23. The new business to be considered will be schedules for flour, ground mustard, and mustard flour, and a reconsideration of the macaroni standards.

MEETING OF ASSOCIATION OF SCIENTIFIC APPARATUS MAKERS

The Association of Scientific Apparatus Makers of the United States of America met at the Bureau of Standards April 21, 1922. The Committee on Standardization of Chemical Apparatus met April 20 and discussed details of elimination of sizes and shapes of apparatus. The committee has been coöperating closely with the Committee on Guaranteed Reagents and Standard Apparatus of the AMERICAN CHEMICAL SOCIETY and is planning to continue work on standardization of dimensions now that the general field of elimination has been covered. The meeting of the Section of Physics and Chemistry was devoted largely to discussion of the report of the Committee on Standardization of Chemical Apparatus and a similar report from a committee on standardization of physical apparatus.

CONFERENCE ON NONFERROUS ALLOYS

A conference of the Advisory Committee on Nonferrous Alloys of the Institute of Metals Division of the American Mining and Metallurgical Engineers with representatives of the United States Bureau of Mines was held at the Bureau of Mines, Washington, D. C., April 25. This was the second meeting held for the purpose of developing a program of coöperation between the nonferrous metal industries and the Bureau of Mines, with especial reference to the nonferrous work of the latter organization. The conference discussed the question of the functions and possibility of development of the proposed Alloys Research Association, now known as the Alloys Research Information Service. The feeling was that, owing to the depressed industrial situation, it would not be a propitious time to push the matter.

NATIONAL RESEARCH COUNCIL APPOINTMENTS

W. M. Corse has been elected chairman of the Division of Research Extension, with W. A. Hamor as vice chairman.

E. W. Washburn has been elected chairman of the Division of Chemistry and Chemical Technology and Charles L. Reese, vice chairman, effective July 1. The chief project of the Division will be the editing of the Critical Tables of Physical and Chemical Constants. Other members of the staff will be announced later.

INTERDEPARTMENTAL CONFERENCE ON CHEMICAL LIME

On Wednesday, May 17, the Interdepartmental Conference on Chemical Lime held its last meeting of the winter and reviewed its year's work. This conference, composed of representatives of each interested department, is preparing specifications for the different kinds of lime used as chemical reagents in various industries. Two of these specifications, "Lime for Use in Cooking Rags in the Manufacture of Paper," and "Quicklime, Hydrated Lime and Limestone for Use in the Manufacture of Glass," have been published as Bureau of Standards *Circulars* **96** and **118,** respectively. Others, in various stages of completion cover the quality of lime used in causticizing, water purification, manufacture of sulfite pulp, depilation of hides, ceramics, etc.

May 15, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Dr. Jacob Lipman of the New Jersey Agricultural Experiment Station, who is now traveling in Europe, delivered two lectures in Paris: the first before the Académie d'Agriculture on the condition of agriculture in the United States, the other before the Société de Chimie Industrielle on the fertilizer industry in the United States. After the lectures, Dr. Lipman answered numerous questions. He replied with exact facts and figures, and the discussions were especially interesting. Messrs. Georges Claude, Matignon, Etienne, director of the Solvay establishments, and Binder, a potash manufacturer, discussed diverse points with the lecturer.

As for nitrogenous fertilizers, cyanamide seems to be condemned because its alkaline dust has an injurious effect on vegetation. Cyanamide factories are being converted for the manufacture of cyanides and other chemical products of industrial importance. In France, the important cyanamide factory, which was established at Nanterre during the war and was controlled by the Service de Poudres, has been released and has gone back to the manufacture of tobacco.

The ammonium sulfate industry is prospering in the United States, and production has surpassed consumption, thus making export possible. Although neither the Claude nor the Haber process is in operation in the United States, it is estimated that when these processes do furnish their share of nitrogen the organic nitrogenous matter hitherto employed can be saved for animal foods.

In France, in spite of the dissolution of the Nitrogen Company (Compagnie l'Azote), the use of the Haber process is again planned. In the Finance Committee of the Chamber discussion has been going on of the project permitting approval of the contract dealing with the manufacture of liquid ammonia. This contract, entered into by Mr. Loucher, minister of the Reconstitution Industrielle, and the Badische-Anilin, had for its purpose the transfer of the Haber process. An important majority of the Committee seem to feel that the Haber process should be finally established at the Toulouse powder factory.

Messrs. Roux and Patard, the latter director general of powders, have shown the importance of our nitrogen requirements, and the Haber process can assure us of a great part of this, rapidly. Besides, Mr. Patard has pointed out to the Société des Ingénieurs Civils characteristics of the Haber process which seem to make it decidedly superior to the cyanamide or arc process for the fixation of nitrogen. For one thing, the hydrogen produced by this process can be used for other purposes, such as the hydrogenation of oils and hydrocarbons. Attempts are at present being made to establish in France factories for the production of hydrogenated naphthalene, as a substitute for turpentine.

In Germany, the production of nitrogen has doubled over what it was in 1913. It has now reached 220,000 tons, 90,000 tons of which are for ammonia. Ammonia production is now 150,000 tons.

As for phosphoric acid, Dr. Lipman's audience was pleased to hear that France and America are now the great owners of phosphate mines: the Americans with the Florida phosphates and the deposits discovered in Wyoming, and the French with their deposits in Tunis, Algeria, and Morocco.

In Germany basic slags contribute a large share of phosphoric acid. This supply has disappeared since the war, as a result of the peculiar condition in the Ruhr valley. Germany is therefore obliged to turn to France or the United States for her phosphoric acid. This is especially difficult for her on account of the rate of exchange.

Dr. Lipman expressed the hope that development in the production of phosphoric acid by the electric furnace would soon be successful. The ease of rendering soluble the phosphorus thus obtained would make possible a considerable decrease in the consumption of sulfuric acid.

Finally, we learned with interest that the efforts made in the United States during the war, to secure to the farmers their minimum potash requirement, are being continued. In spite of this, we estimate that America has every advantage in supplying herself with potash in the European market. We know that in France we can furnish the American market in competition with Germany.

At the suggestion of Mr. Binder, the meeting passed a resolution that in the final disposal of the Alsatian mines, an appeal be made, to a certain extent, to American capitalists. By this means we can assure ourselves of a large outlet in the market.

The total 1921 production of potash was 902,126 tons, almost tripling that of 1913.

Evidently, the German potash mines comprise 200 shafts, while the Alsatian mines comprise only 17, but this great number of shafts seems to be a stumbling block for the German industry which will make it difficult to struggle with Alsatian potash. The German mines cannot now work with a full yield. There is a scattering of energy and workmanship to maintain the mines in activity, which is rather detrimental.

The progress in the sale of Alsatian potash in the first three months of 1921 was 46 per cent, while that of the German potash reached only 26 per cent.

All who attended the meetings expressed the desire that American scientists should come frequently to discuss with us their work and the industrial condition of their country.

Natural and Cultivated Pearls

The French pearl market is greatly disturbed by the appearance of a great number of cultivated pearls of Japanese origin. In the scientific societies there has been much discussion of the means of distinguishing natural from cultivated pearls. Although the two kinds are identical from the biological point of view, they do not possess the same market value.

All the tests so far proposed have given uncertain results. Mr. Salibourg seems to have solved the problem by examining the interior of the pearl microscopically with very strong illumination. The pearl always has an orifice for the purpose of mounting. By closing this orifice and placing over it a very small metallic mirror consisting of a tiny globule of mercury which functions as a convex mirror, an image, and consequently a photograph, can be obtained of the cylindrical axis of the pearl through the orifice. With a natural pearl a homogeneous circle is obtained, but in an artificial pearl this circle bears concentric striae, corresponding to various stages of its enrichment by culture.

Index of Toxicity of Combustion Gases

The ever-increasing use of explosion motors and generator gas motors, on the one hand, and the diversity of origin of the coal now consumed in France, on the other, have led hygienists, in view of several gas-poisoning accidents, to study the combustion gases produced under diverse conditions.

Mr. Kohn-Abrest, the distinguished director of the toxicological laboratory of the city of Paris, proposes to call the ratio $CO:CO_2$ the "index of toxicity." He determines carbon monoxide by absorption in blood, and carbon dioxide by transformation to barium carbonate.

The index of toxicity is very high in combustion products from explosion motors. It amounts to 1.40 to 2.09. In the products of the combustion of coal the index varies enormously with the nature of the supporter of combustion. This is also true with the different kinds of lighting apparatus and of gas heaters, where the index varies with the construction of the apparatus.

Mr. Kohn-Abrest proposes to prohibit for domestic use all apparatus with an index higher than 0.01, a value beyond which the atmosphere produced becomes rapidly dangerous.

Franco-German Dye Alliance Denied

Various journals have echoed the information announcing an alliance between French dye industries and German factories.

This would amount to an economic and technical collaboration, by which the German factories would send to France their technical men and chemists to establish factories. The French, on their part, would limit their production to their needs, and would turn over a part of their profits to German manufacturers.

This information, which seems to put the French industries under the complete control of German dye manufacturers, has been formally denied, and the political situation at the present time tends to show its falsity.

April 28, 1922

CANADIAN LETTER

By T. Linsey Crossley, 208 King St., West, Toronto, Ontario

Inaugurating this Canadian letter the writer feels that his name should not appear at its head, without the admission that our far-flung provinces and generously spaced centers of scientific activity make a resort to collaboration necessary in order to provide a survey that shall not be confined to the limited vision of an observer in one locality. The writer's duty will be, therefore, to review activities as reported to him from the various centers.

To some of the readers of This Journal the mention of chemistry in Canada may bring to mind only McGill and Toronto Universities. All the provinces now have universities with chemists and chemical engineers in fair number engaged industrially.

In the extreme West, British Columbia has two chemists' associations, the British Columbia Chemists' Club, and the Pacific Section of the Society of Chemical Industry. These two organizations, with the students' Chemistry Club of the University of British Columbia, recently united in an expeditionary meeting to two of Canada's newest chemical industries, the Triangle Chemical Company of New Westminster, and Acetate Products Ltd. of South Westminster. These concerns making sulfuric and hydrochloric acids, fertilizer and wood distillation products, mark the western development of forms of chemical industry, based on the very marked trend to more scientific agricultural development in the Dominion and the utilization of wood species that grow rapidly and numerously in sections where the merchantable timber either does not grow or has been removed. The elder, which grows prolifically on the Pacific slope and to a diameter of a foot or more, is the tree utilized in this Western development. It is not generally known that at Basque, British Columbia, a deposit of natural pure magnesium sulfate has been developed commercially for some time, from which it has been found possible to ship material as mined, running as high as 98 per cent. It is likely that the lower grades will be treated by recrystallization. This deposit is perhaps unique in America.

For some years there have been endeavors to create an Institute of Research at Ottawa with the financial backing of the federal government. There were discussions by advocates of two views, one that the institution should be at the center of government, the other that it should be located at a scientific center, or that branches should be established at the leading universities and industrial centers, to act as foci for specific types of work. Last year the recommendations of the Advisory Research Council were embodied in a bill which passed the lower house, but was thrown out in the Senate. The present government upon taking office was approached and has recently decided to table the matter for this year. There seems to be a body of opinion growing that as far as governments are concerned not much may be expected.

Ontario engineering bodies have presented a bill to the provincial legislature whereby all professional engineers must be registered. Chemists have been included in the requirements of the act, and the fact that they, therefore, would be technically known as Registered Professional Engineers and not as chemists has raised a great deal of discussion as to the use of the word chemist. The only legal status of "chemist" in Ontario is that synonymous with apothecary, druggist or pharmacist. It is expected that the bill will meet many difficulties in the Committee stage, being objectionable to certain agricultural and labor interests.

The annual convention of Canadian chemists at Ottawa, May 16 and 17, will have passed into review ere this contribution appears. To one who has been in touch with chemical work in Canada for the last twenty-five years, it means much to note the numbers and good fellowship of these meetings. Canadian industries have developed along scientific lines and the chemist in Canada feels, therefore, that he is an economic entity. In 1900, for example, the pulp and paper industry in Canada employed three chemists and one of them was dispensed with because the manager said he was in the way. This industry now employs over forty chemists and has become one of the leading industries in the matter of scientific control and investigation.

A meeting was held in Toronto, April 28, of which the result was a resolution to form a Canadian Metric Association. A temporary committee was formed to draft a constitution and inaugurate action toward more definite efforts to popularize the system for the benefit of science and industry.

General business conditions have not for some time been favorable to chemistry and chemical engineering. These have suffered in some measure by the closing down or curtailing of business in some of the larger industrial and metallurgical works. The situation now, however, leads to a legitimate optimism.

May 9, 1922

The Forest Products Laboratory

The committee in charge of the Decennial Celebration which was held at the Forest Products Laboratory, Madison, Wis., July 22 and 23, 1921, has concluded its activities with the publication of a book entitled "The Forest Products Laboratory: A Decennial Record." The book recounts the need of centralization of research on forest products which led to the establishment of the laboratory, and describes the researches which were carried out in the period before the war, the work of the war years when the staff increased from 84 to 458 workers, and the developments since the war, together with the fields of research which lie open for the future.

The estimated financial value of the research results obtained is of considerable interest. The total amount appropriated for the laboratory during its ten years of life is close to two million dollars. Of this amount, the war period accounts for a large portion. The annual saving in the building and construction trade, for instance, as a result of the work at the laboratory on the mechanical properties of American woods which made possible a 20 per cent increase in allowable working stresses in structural timbers, is estimated at $4,000,000. Since the lumber used annually in this trade is worth roughly $200,000,000, the saving theoretically possible is $40,000,000. As another example, the adoption of improved methods of turpentining developed by the laboratory has resulted in increased yields and decreased injury to timber with net savings aggregating $4,000,000 per year. The annual saving to American industries directly attributable to the work of the laboratory is estimated at approximately $30,000,000. A much larger saving would be made if full use were made of the results of its investigations.

Inventions by Government Workers

A committee of representatives of British governmental departments and leading British scientists has recently recommended to the Hon. A. J. Balfour, Lord President of the Council, a comprehensive scheme of dealing with inventions by government workers or by individuals aided or maintained from public funds.

The committee recommends the organization of an Interdepartmental Patents Board. Pending a decision in each case by this Board, all rights in inventions made by government employees shall belong to the government. If the inventor can satisfy the Board that he derived no assistance from the nature of his employment in making the invention, he shall be entitled to all rights therein. The question of whether the inventor is entitled to any reward in addition to the enjoyment of commercial rights shall be decided by the Board. Where the rights in an invention capable of commercial exploitation belong to the government, the invention shall be exploited commercially for the benefit of the government.

A system of awards and merits for the inventor is proposed, which should be passed upon by an Awards Committee, to be organized within the proposed Patents Board. These are not intended as substitutes for commercial profits, but as a recognition of merit and as an incentive to government workers.

The Canadian Institute of Chemistry has just issued a compact little book which lists officers, committees, and members of the council, gives a brief historical sketch of the Institute, the constitution and by-laws, and names and addresses of members, corrected to December 31, 1921.

Personals

Mr. Charles W. Schaffer resigned as chemist at the National Aniline and Chemical Company to become associated with the Central Dyestuff and Chemical Company of Newark, N. J.

Mr. Harry E. Rice has severed his connection with the R. R. Donnelley and Sons Co., Printers, of Chicago, where he has been employed for several years in the capacity of chemist. He is now in charge of research and development work for the American Printing Co., also of Chicago.

Dr. J. C. Witt has been appointed a consulting chemist in the Bureau of Mines, and from time to time will coöperate with that Bureau in the study of some phases of portland cement manufacture.

Mr. H. E. Otting has resigned his position as superintendent of the laboratories of the Nestles Food Company of New York City, to accept a similar position with the Mohawk Condensed Milk Company of Chicago with his headquarters at Corry, Pa.

Dr. Martin S. Kissel, Jr., has just returned from China, where he was chief chemist of the Sun Cheong Milling Co., and has opened a laboratory, 603 Linwood Street, Brooklyn, N. Y.

Mr. Lloyd A. Bosworth recently resigned as a chemist in the Analytical and Research Department of The Drug Co., Boston, Mass., to accept the position of chief chemist for the Patent Cereals Co., Geneva, N. Y.

Mr. Henry P. Busch, in charge of the laboratories of Shoemaker and Busch, has been elected a director of the United Security Life Insurance and Trust Company of Philadelphia.

Mr. Pierre E. Haynes, formerly with The Linde Air Products Company and The Prest-O-Lite Company, announces the establishment of a consulting engineer's office in Buffalo, N. Y. Mr. Haynes will be associated with Haynes and Mote, Public Utility Counselors of Indianapolis, Ind.

At the annual meeting held at the company's offices, February 14, in Detroit, The Digestive Ferments Company elected **Howard T. Graber** secretary of the corporation. Mr. Graber assumes his duties of secretary immediately and retains his former duties as Director of the Chemical Laboratory and Chairman of the Publicity Committee.

Mr. L. J. Buck has severed his connection with the National Carbon Company and has beoome U. S. Sales Representative of the British America Nickel Corp., Ltd., Ottawa, Canada, with offices in the Canadian Pacific Building, 342 Madison Ave., New York, N. Y.

Mr. Clayton L. Jenks has opened an office at 2 Rector St., New York, N. Y., and will give especial attention to chemical and mechanical inventions, the correction of improper usage of trademarks, and the organization of patent departments. Mr. Jenks was for six years an assistant examiner in the U. S. Patent Office, and organized and conducted a patent department for Eastman Kodak Co., at Rochester, N. Y., and also established a similar system for Norton Company at Worcester, Mass., of which he will retain charge.

Mr. Robert D. Landrum has left the employ of Harshaw, Fuller & Goodwin Co., Cleveland, Ohio, to enter business for himself as vice president in charge of development and sales for the Vitreous Enameling Co. and the Vitreous Steel Products Co., of Cleveland.

Mr. Lewis I. Birdsall of Minneapolis has been appointed the representative of the American Chemical Society to act on the committee being formed by the Surgeon General of the Public Health Service to pass upon a standard for drinking water used by common carriers operating in interstate traffic, to review the present standard of the Treasury Department and to recommend a standard or standards based on recommended specific methods of laboratory analysis and field survey which will be applicable to all classes of water supplies coming within the supervision of the Interstate Quarantine Regulations of the United States.

Mr. James G. Vail, Chairman of the Philadelphia Section of the American Chemical Society, delivered a lecture before the National Association of Corrugated and Fiber Box Manufacturers at St. Louis on April 19. His topic was "Silicate of Soda as an Adhesive."

Mr. D. D. Berolzheimer, Assistant Technical Editor of the Chemical Engineering Catalog and co-author of the Condensed Chemical Dictionary, has been appointed Manager of the Information Bureau of The Chemical Catalog Co., Inc., and of that of the Service Department of This Journal.

Industrials

The N. & G. Taylor Co., Philadelphia, Pa., manufacturers of tin plate, have resumed operations in the open hearth and bar mill departments of their Cumberland plant, while operations in the black plate and tinning departments are now approximately 90 per cent of capacity. A good demand for roofing tin, especially in the higher grades, is reported, and the tin plate business of the district continues to improve.

The Paul Maehler Company has recently issued a booklet, well illustrated, which describes in some detail the special features of the ovens, and their application to various types of industrial use. Ventilation and circulation, fuels for industrial ovens, and conveyor and special type ovens are among the topics discussed.

The Electro Metallurgical Sales Corporation has prepared a very attractive booklet which describes various products of the electric furnace and their uses in the fields of ferrous and nonferrous metallurgy, together with interesting historical data in regard to the development of these products. High and low carbon ferrochrome and miscellaneous chromium alloys, ferrosilicon of various grades, ferromanganese, and zirconium alloys are treated in turn, including applications and typical analyses.

E. I. du Pont de Nemours & Co., Wilmington, Del., have permanently closed their historic powder mills at Brandywine, and the plant will be dismantled. The Brandywine mill was the first of its kind in this country and furnished munitions for the War of 1812 and the Civil War, and has been used continuously for the manufacture of powder and explosives up to a recent date.

Articles of incorporation are being prepared for a new chemical concern in Cincinnati, the principals of which are Robert W. Hilton, former vice president of the Ault & Wiborg Co., and now consultant chemical engineer, and A. Brooking Davis, assistant general manager of the Cincinnati Chemical Works, Inc. The new company will operate research and technical laboratories fitted for the development of factory processes and patents, and for general consultation to the chemical and related industry, and will also manufacture a selected group of the finer chemical products.

The first large freighter to be loaded entirely with Celite products recently left Port San Luis, Cal., bound for Atlantic ports by way of the Panama Canal. Two other vessels are to follow, this being the first time that three entire vessels have been used to the exclusion of other products. In spite of the necessity of shipping by motor truck to the Pacific Coast Railroad and the rehandling involved, it has been found that this method of water shipment reduces the final cost of the products to an appreciable extent.

The American Trona Corporation has reopened its potash plant at Searles Lake, Cal., which had been closed for about a year. Officials of the company say that they wish to accumulate a stock of potash, since contracts are made by the year, and that they will offer domestic goods as low as imported.

The Raymond Bros. Impact Pulverizer Company has established a new permanent western office at 1002 Washington Bldg., Los Angeles, Cal., in charge of W. B. Senseman.

The receivers of the Butterworth-Judson Corporation have taken possession and are continuing the business as directed. They expect to complete unfilled orders and to accept new orders in usual course.

The American Dyes Institute has sublet its office rooms in New York and the office force is to be disbanded. Mail for the Institute should be addressed in care of the Dye Section of the Synthetic Organic Chemical Manufacturers Association, One Madison Ave., New York City.

A large deposit of genuine chalk cliffstone whiting which is claimed to be equal if not superior to the imported grade of chalk, has recently been located at White Cliffs, Ark. The property, comprising over 2900 acres, has been purchased by the Krippendorf-Tuttle White Cliffs Products Co., recently organized, and machinery and equipment are now being installed at the new plant.

Devoe and Reynolds have established a school of instruction as an aid to up-to-date merchandising, which is attended by all classes of employees. Regular lessons are given out for study covering the making of paints, the properties of drying oils, the application of paints, and many other matters of interest to the industry. Weekly lessons will be continued until the end of June.

BOOK REVIEWS

Pulverized Coal Systems in America. By LEONARD C. HARVEY. Revised edition; paper $7^1/_2 \times 9^3/_4$; iii + 115 pp., 25 illustrations. Department of Scientific and Industrial Research, Fuel Research Board, Special Report No. 1. Published by His Majesty's Stationery Office, London, 1922. Price, 5s. 0d. net.

This is a revision of the original report prepared by Mr. Harvey after his return to England from a three months' survey of pulverized coal systems in America in 1918. The new edition includes a brief review of progress in America during the last two years as obtained from questionnaires sent to a large number of users of pulverized coal, and from a short subsequent visit to the United States. Brief reference is also made to recent progress in England and other countries as a resultant of the pioneer work carried out in America.

In a prefatory note Sir George Beilby, Director of the Fuel Research Board, states that America burns between ten and fifteen million tons of coal per annum in pulverized form, while its use in Great Britain has been extremely limited and the progress most disappointing.

The report consists of seven chapters and five appendices covering the following subjects: conditions with pulverized fuel, range of fuels suitable, coke, pitch, anthracite, bituminous coals, utilization of waste coal, lignites and peat; cost of installation and cost of powdered coal; standard mill house practice and tabulated answers given on questionnaire sheets sent to American users of pulverized coal; transportation of coal dust to burners; pulverized coal storage and spontaneous combustion; feeders, mixers and burners; applications, opinions of users, working results, metallurgical and similar processes, open hearth steel melting furnaces, heat treatment and soaking pits, welding and puddling furnaces; steam boilers; railway locomotives; marine propulsion; domestic and office buildings; central heating systems investigated by the author in 1918 and new systems; installations visited by the author in 1918; list of pulverized fuel users; difficulties in the use of pulverized coal; and an excellent bibliography compiled by the Engineering Societies' Library.

The chapter on cost of installation and operation of pulverized coal plants is very useful. A table is given of the number and size of dryers and pulverizers, including hours of labor for tonnages ranging from 5 to 1000 tons per day. The answers to questionnaires sent to fifteen American users of pulverized coal give such information as kind and analysis of coal used; type and number of boilers; type and number of metallurgical furnaces; pulverizing plant equipment; and comments by the users on the success or failure of the systems installed at their plants. A brief but comprehensive description is given of the operating steps from the raw coal to the pulverized storage bin with discussion of the advantages and disadvantages of different transportation systems and pulverizers. The author could well have given more space to safety rules for the prevention of dust explosions and fires in pulverized coal systems. Mr. Harvey states that in order to conserve the volatile constituents in drying pulverized coal, precautions need to be taken to insure that no part of the coal reaches a temperature higher than 200° C. To avoid danger of firing, the maximum temperature should probably not exceed 125° C.

Chapter 6 contains a variety of valuable information obtained from questionnaires and other sources on the use of pulverized fuel in both the ferrous and nonferrous metallurgical industries and, in particular, operating data on steam boiler installations, including tests of boilers at the Missouri, Kansas & Texas Railroad Shops at Parsons, Kans.; at the Oneida Street Station of the Milwaukee Electric Railway & Light Company, Milwaukee, Wis., and railway locomotive tests on the Great Central Railway.

The report is replete with data and illustrations and is undoubtedly one of the best contributions to this subject.

A. C. FIELDNER

The Distribution of Gas. By WALTER HOLE. 4th edition, revised and enlarged. 699 pp. Benn Brothers Ltd., 8 Bouverie St., E. C. 4, London, 1921. Price, 50s. net.

A review of this edition of the "Distribution of Gas" merely strengthens the impression of thoroughness exhibited in the previous edition. The book should be of interest to all distribution engineers, even though the practice it represents is somewhat different from that generally prevalent in America. Primarily, the book describes English distribution practice, and is written for English gas engineers; a fact that must be kept in mind by the American reader in order that he may derive the greatest benefit from it. However, it is apparent that Mr. Hole has not failed to supplement his experience, or that of his associates, in order to strengthen the book when he thought it necessary or advisable, by reference to American or other practice.

From an American point of view, it is felt that the book should more rightly have been called the "Distribution and Utilization of Gas," since nearly one-third of the subject matter is devoted to methods, equipment and appliances dealing with the use of gas. In America, except in quite small companies, the engineer in charge of distribution has but little to do with the utilization of gas, except for the connection of the appliances, and consequently, his knowledge of what is probably the most important feature of the gas industry, that is, the giving of satisfactory and comprehensive service to the user of gas, is quite limited.

For this reason, Mr. Hole has performed a valuable service in inseparably tying up the subject of utilization with that of distribution. Since the responsibility of the distribution engineer should not cease until the gas is satisfactorily functioning, he should know as much as possible regarding the principles of combustion and the proper application of these principles to the "thousand uses of gas." In this book he will be reasonably certain to find information on all phases of this subject clearly set forth.

Likewise, the same thought may be extended to include the chapter on compressors and boosters. Too little information is available on this subject, but it is unquestionable that wherever so-called medium or high pressures are to be carried on the distribution system, the distribution engineer should be familiar with these features.

It is to be expected that in many instances the American gas engineer will find methods for accomplishing distribution work which are more or less different from those with which he is familiar. The discovery of these differences should not make him discard the book as containing information not applicable in his situation, but should make him find out whether or not his own method of doing the work is the more satisfactory.

It is by the study of such a book that American gas engineers may broaden their knowledge and experience, and for this reason the book is recommended to them. Mr. Hole is to be congratulated on his work.

C. E. REINICKER

Distillation Principles and Processes. By SYDNEY YOUNG (with the collaboration of E. BRIGGS, T. HOWARD BUTLER, THOS. H. DURRANS, F. R. HENLEY and JOSEPH REILLEY). 509 pp. Macmillan & Co., Ltd., New York, 1922. Price, $10.50.

Young's "Fractional Distillation" has been the standard English text on the theory of distillation since it was published in 1903. The present volume is a reprint of the 1903 edition with some revisions and with the addition of six sections on manufacturing processes involving distillation, each written by a man who was especially familiar with the process described. These sections give general rather than particular engineering data on the different types of distillation apparatus in use, and each section gives a practical example of some phases of the theory of distillation or, as in the treatment of fermentation in the section on acetone and butyl alcohol, of some process closely related to distillation. The section on alcohol goes into the theory of the separation of small proportions of impurities by distillation in addition to describing the usual forms of alcohol distillation apparatus.

It is interesting to note that most of the examples of modern plants described in the section on petroleum are taken from California practice.

The section on tars summarizes the whole subject of production and treatment, including the methods of separating and purifying tar products by distillation.

In the section on glycerol are described the types of glycerol stills in use, and some figures on yields and power costs are given.

The theory of steam distillation is well treated in the section on essential oils.

The reviewer considers the book the best that has yet been published on the general subject of distillation, and he makes this statement in spite of the fact that neither Young nor his collaborators have given a satisfactory theoretical treatment of the subject of separation of materials in a fractionating column. We do not understand how Young could have so ignored the work of Sorel and of Hausbrand as to miss completely the definite relationship between the expenditure of heat and the separation of materials effected in a section of any fractionating column, yet nowhere in the present volume is this relationship brought out, and all of Young's collaborators are equally hazy when describing what takes place in a fractionating column. While no book on distillation that does not give a thorough treatment of the theory of fractionating columns can be considered complete, the present book partly makes up for this lack by its excellence in all other respects, and the reviewer considers it invaluable to anyone interested in distillation, either in the plant or laboratory.

W. A. PETERS, JR.

Gas Chemists' Handbook. Compiled by Chemical Committee Technical Section, AMERICAN GAS ASSOCIATION. 608 pp. American Gas Association, 130 East 15th St., New York, 1922. Price, $6.00 in the United States and Canada, $6.50 in foreign countries.

As might be expected from the able list of collaborators, this is an excellent volume and a great improvement over the first edition. The sections dealing with tar, light oil, water analysis, lubricants, refractories, gas analysis, and ferrous metal are clear and complete, though the last two are perhaps a trifle long for such a work.

The chapter on coal and coke is well arranged and on the whole satisfactory. The methods for sulfur in coal do not, however, mention Parr's sulfur capsule in which the charge is exploded by heating in a flame; this gives a more certain combustion, especially in the case of cokes. Volumetric methods for sulfur are also omitted, and the sulfur is precipitated without removal of iron.

The work on gas oil is complete, specific, and accurate, though there is some doubt as to whether a glass condenser should stand cold water till the temperature of the distillate is 600° F.

The discussion of calorimetry is old and subject to question. The difference between the temperature of the room and inlet water should be nearer 2° than 5°, and it is a poor observer indeed who cannot check his results within less than 10 B. t. u. No mention is made of the stem correction as such, or of the correction for the efficiency of the instrument.

In the part dealing with weak ammonia liquor, it might have been stated that *p*-nitrophenol is a better indicator than methyl red or cochineal, but the method for free ammonia in strong liquors is good. In the determination of active lime, it would seem that more precautions should be taken to prevent access of carbon dioxide, and it might have been better to recommend wheat starch in place of the soluble variety. For cyanogen in gas, there is a better method than the one given, and the method for naphthalene in gas is slow and inaccurate, especially with small amounts of naphthalene.

Many will disagree with the method for the valuation of oxide, and in the determination of lime in new oxide, the volumetric method is not mentioned. The section dealing with paints is excellent, with one exception; the extraction method given is not satisfactory. This should be done in a thimble in a Soxhlet. The treatment of pipe deposits is incomplete; for instance, a method should be given for moisture alone. Neither does it seem advisable to dry naphthalene at 105° C.

A number of printer's errors are noted, as in the definition of the initial set of cement, and in some of the figures.

Most of the above criticisms would, however, probably apply to any handbook of this nature, and the work as a whole is very valuable and heartily to be commended.

C. H. STONE

Les Métaux Precieux. By JEAN VOISIN. 264 pp. J.-B. Baillière et Fils, 19, Rue Hautefeuille, Paris, 1922. Price, paper, 25 fr.; flexible cover, 35 fr.

This volume constitutes one of the series of the Encyclopedia of Industrial Chemistry, published under the direction of M. Matignon.

The metals treated are gold, silver, platinum, and the other platinum metals. The first chapter is devoted to gold assaying; a resumé of its physical and chemical properties; the occurrence of gold in nature; the mining regions and their production, methods of exploitation, and treatment and refinement of the minerals.

The same subjects are treated with reference to silver in Chapter 2; and platinum and platinum metals in Chapter 3. Chapter 4 is devoted to the economics of the precious metals; Chapter 5, to coinage, jewelry, and methods of assay; Chapter 6, to the application of the precious metals in the different industries, including silver and gold plating, metallurgy of platinum, application to the electrical industries, medicinal uses, manufacture of platinum ware, application of platinum to catalysis and to photography, and finally, a discussion of the treatment of industrial residues.

Gay-Lussac tables are also given for the calculation of silver assays by means of sodium chloride and silver nitrate. This volume contains a great deal of material of interest to metallurgists and others interested in the precious metals. On account of the variety of subjects treated in a limited space, many of the discussions are of a rather cursory nature.

The statistics on the production of the precious metals are for the most part brought down only through 1914, although the world's production of silver and gold are carried through 1918, and platinum through 1917. The chapter on the economics of these metals, giving detailed statistics as to the variation of prices of gold and silver in Paris during recent years, through 1920, is perhaps the most interesting one in the volume.

S. C. LIND

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

April

The **mining industry** of Algeria during 1921 was seriously affected by a dull market coincident with an appreciable reduction in the prices of metals. **Phosphate** was the one exception, shipments thereof being larger than in 1920. (Pp. 16–7)

The new motion-picture film, "The Story of an Electric Meter," produced under the direction of the Department of Commerce in coöperation with the Sangamo Electric Co. of Springfield, Ill., is rapidly nearing completion. It shows in a graphic way the steps in the manufacture of an **electric meter,** as well as its many uses. A feature of the film will be the animated drawings showing complete operation of the meter itself. When completed it will be given the widest possible circulation by the Government. (P. 24)

The trade of the United States in **petroleum** products in February is reviewed. (Pp. 33–4)

The total production of **chemical wood pulp** in Norway in 1921 was much less than in 1920, being estimated at 150,000 tons, compared with 224,000 tons in 1920. (P. 36)

Owing to various decrees restricting the export of **wood pulp** and to stagnation in the paper manufacturing industry in Portugal, the output of wood pulp has been greatly reduced for the past two years. (P. 37)

Operation of the deferred duty of the new Australian customs tariff has been postponed on **citric acid** from March 31, 1922, to June 30, 1922. (P. 51)

Recent amendments to the Customs Tariff of the Federated Malay States increases the import duty on **petroleum.** (P. 51)

Italy, in a recent ministerial decree, granted an exemption from import duty on **alcohol** to be used in making medicated soap. (P. 53)

The discovery of **platinum** in Brazil is reported. (P. 60)

Germany has recently concluded contracts for the delivery of 800,000 tons of **phosphoric ore** from Newfoundland. It is calculated that it will be possible to procure about 1,000,000 tons per annum of this ore from Newfoundland or Labrador. (P. 75)

The possibility of modern application of **iodine** to industrial processes would seem to warrant a thorough extraction of the material and the lowering of prices to a commercial scale. The present Chilean arrangement requires that all iodine contained in the ore whose extraction is not permitted by the quota assigned the plant be thrown away and lost entirely. It is estimated that from 10,000 to 14,000 tons could be produced if all the iodine contents of the treated ore were recovered. (P. 112)

The Northern Peru Mining and Smelting Co. has undertaken new mining operations which constitute the most important mining development in Peru for a number of years. Their activities have to do especially with **copper** and **coal.** (P. 113)

The use of **fertilizers** in Japan is described, and statistics are given showing the production, consumption, and importation of fertilizers. The use of fertilizers in Japan is becoming increasingly important because of the necessity to produce crops sufficient to feed a rapidly growing population from a very limited amount of arable lands. (Pp. 114–5)

The large factory for the manufacture of **soda** and by-products by the Société Industrielle de Chimie d'Extrême-Orient is practically completed. It represents an expenditure of 11,250,000 francs. The company expects to supply a large number of paper, glass, soap, and spinning factories in the Orient with caustic soda and other chemicals. (P. 116)

The Polish Ministry of Provisionment has prohibited the manufacture of **alcohol** from grain. (P. 120)

Latvia is using **peat** as fuel in its state institutions. (P. 121)

It is reported that a promising prospect for **manganese ore** has been discovered and is being opened in Wales. (P. 147)

A recent experiment at Liverpool for disinfecting **anthrax-infected wool,** if successful, will reduce the cost of sterilizing from 1.5d. per pound to 0.25d. The new apparatus employs a combination of X-rays and ultraviolet rays. (P. 148)

During the year 1921 Great Britain imported 1,175,446,296 gal. of **petroleum,** of which one-half came from the United States. (P. 166)

The exploitation of **petroleum** in Venezuela is described. (Pp. 166–7)

The present export duty on **oil,** as well as the special taxation on mining products, from the Dutch East Indies has been recommended for discontinuance. (P. 178)

A new Chilean law provides for a surtax on all imports of **oil** from those countries imposing an export tax on such products. (Pp. 178–9)

The Bureau of Foreign and Domestic Commerce has on file a report on the market for American **paints** in Cuba. (P. 185)

The existence of **minerals,** such as bauxite, limestone, red ocher, iron pyrites, mica, and magnetic iron ore is reported in British Honduras. (P. 185)

The Japan Dyestuff Co., since its establishment, is said to have produced about 100 different kinds of **dyes,** of which 40 are already on the market. (P. 186)

A firm in Manila is anxious to communicate with paint and varnish manufacturers in the United States interested in the purchase of light-colored grades of **gum copal.** The name of this firm can be procured from the Bureau of Foreign and Domestic Commerce. (P. 186)

A method of securing dye from **kaoliang bran** has been discovered by mixing it with soda, sulfate, etc. The brown and black dyes produced by this process have been patented and a patent to cover blue-black has been requested. (P. 186)

The sources of **thorium** in Ceylon are described. (Pp. 186–7)

The **petroleum** trade and industry in Belgium is reviewed. (Pp. 205–6)

A bed of **magnesite,** 15 mi. in length, 1 $^3/_5$ mi. wide, and with a height of about 500 ft. above the level of the ground, is reported to exist in Manchuria. The deposit is said to have an estimated reserve of 20,000,000 tons. (P. 219)

In February, with only 24 working days, the production of **iron ore** in Meurthe-et-Moselle, France, amounted to 541,000 metric tons, as compared with 527,000 tons in January. (P. 219)

It is reported that if chemical and mechanical processes supersede the primitive processes now employed, native Brazilian **fibers** may replace jute in the preparation of thread for spinning. (P. 220)

According to a published report, the West Australian Forest Products Laboratory and the Commonwealth Institute of Science and Industry have been authorized to conduct experiments on a semicommercial scale, with a view to determining whether it is possible to produce a **paper pulp** from Australian timber. (P. 235)

The Italian government has removed the restrictions on the **exportation** of all chemical products. (P. 247)

The **mineral** production of Ecuador is reviewed. (P. 250)

The **mining** industry for 1921 in New South Wales is briefly reviewed. (P. 256)

An investment opportunity for American capital is offered in the **mica** fields of South Africa. (P. 260)

STATISTICS OF EXPORTS TO THE UNITED STATES

CONSTANTINOPLE—(P. 121)
Borate stone
Gum tragacanth

SMYRNA—(P. 122)
Chrome ore
Gum tragacanth
Licorice root
Licorice paste
Olive oil

SALONIKI—(P. 122)
Saffron

TAMPICO—(P. 207)
Petroleum

AUSTRIA—(P. 207)
Ozokerite

FEDERATED MALAY STATES—(P. 219)
Tin

NOGALES, SONORA—(P. 250)
Minerals
Metals

ATHENS—(P. 253)
Chrome ore
Olive oil
Tartrate of lime

CURRENT PUBLICATIONS

NEW BOOKS

Basic Slags and Rock Phosphates. G. S. Robertson. Cambridge Agricultural Monographs. 120 pp. Price, 14s. Cambridge University Press, London.

Catalytic Action. K. George Falk. 146 pp. Price, $2.50. The Chemical Catalog Co., Inc., New York.

Chemical Education: Report of Committee on Chemical Engineering Education, American Institute of Chemical Engineers, 1922. A. D. Little, *Chairman.* 22 pp. Price, $0.75. American Institute of Chemical Engineers, Polytechnic Institute, Brooklyn, N. Y.

Chemistry: Les Actualités de Chimie Contemporaine. A. Haller, Editor. 320 pp. Illustrated. Price, 12 fr. Octave Doin, Paris.

Chemistry of Essential Oils and Artificial Perfumes. Ernest J. Parry. Vol. II. 4th edition, revised and enlarged. 366 pp. Price, 22s. Scott, Greenwood & Son, London.

Chemistry of the Non-benzenoid Hydrocarbons. Benjamin T. Brooks. 612 pp. Price, $7.00. The Chemical Catalog Co., Inc., New York.

Chemistry: Chimie Élémentaire. E. Péchard. 468 pp. Illustrated. Price, 12 fr. 50. Dunod, Paris.

Chemistry: Lehrbuch der Chemie. Vol. I. Stoffe. Max Trautz. 534 pp. Price, 22s. 6d. Vereinigung Wissenschaftlicher, Berlin and Leipzig.

Colloids: Beiträge zu einer Kolloidchemie des Lebens. Raphael Ed. Liesegang. 39 pp. Illustrated. Price, 10 mk. Th. Steinkopff, Dresden and Leipzig.

Colloids: Kolloide Lösungen. Joachim Leimdörfer. 108 pp. Price, paper, 65 mk., plus tax. H. Ziolkowsky, Augsburg.

Concrete and Reinforced Concrete. W. Noble Twelvetrees. 147 pp. Price, 3s. net. Sir Isaac Pitman & Co., London.

Construction: Cours d'Analyse et d'Essai des Matériaux de Construction. A. Anstett. 238 pp. 32 figures. Price, 18 fr. Léon Eyrolles, Paris.

Cyaniding Gold and Silver Ores: A Practical Treatise. H. Forbes Julian and Edgar Smart. 3rd edition. 417 pp. Illustrated. Price, $12.50. J. B. Lippincott Co., Philadelphia.

Dictionary of Applied Chemistry. Vol. III. Explosives—K. Sir Edward Thorpe. Revised and enlarged edition. 735 pp. Price, 60s. Longmans, Green & Co., London.

Dyes Classified by Intermediates. R. Norris Shreve. 632 pp. Price, $10.00. The Chemical Catalog Co., Inc., New York.

Encyclopedia: Enzyklopädie der Technischen Chemie. Fritz Ullmann. Vol. 10. 726 pp. Price, 350 mk. Urban and Schwarzenberg, Berlin.

Fluidity and Plasticity. Eugene C. Bingham. International Chemical Series. 435 pp. Illustrated. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

Handbook of Industrial Oil Engineering. John Rome Battle. 1131 pp. Illustrated. Revised edition. Price, $10.00. J. B. Lippincott & Co., Philadelphia.

Ink: Praktische Handbuch der Tintenfabrikation. Louis Edgar Andés. 223 pp. Price, 36 mk. A. Hartleben, Wien and Leipzig.

Ink: Die Tinten-Fabrikation. Sigmund Lehner. 224 pp. Price, 36 mk. A. Hartleben, Wien and Leipzig.

Inorganic Chemistry. T. Martin Lowry. 943 pp. Illustrated. Price, $9.00. The Macmillan Company, New York.

Mechanical Stokers. Joseph G. Worker and Thomas A. Peebles. 258 pp. Price, $3.00. Illustrated. McGraw-Hill Book Co., Inc., New York.

Metric System for Engineers. Charles B. Clapham. The Directly-Useful Technical Series. 181 pp. Illustrated. Price, $6.00. E. P. Dutton & Co., New York.

Organische Molekülverbindungen. Paul Pfeiffer. 328 pp. Price, 148 mk. F. Enke, Stuttgart.

Paper: The Manufacture of Pulp and Paper. Vol. III. Preparation and Treatment of Wood Pulp. Joint Executive Committee on Vocational Education Representing the Pulp and Paper Industry of the United States and Canada. 691 pp. Illustrated. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Petroleum: Recherche et Exploitation du Pétrole. Jean.-A. Hardel. 276 pp. Illustrated. Price, 16 fr. Dunod, Paris.

Process Engraving. Edward S. Pilsworth. Illustrated. Price, $2.00. The Macmillan Co., New York.

Qualitative Analysis: Anleitung zum Studium der Chemischen Reaktionen und der Qualitativen Analyse. Friedrich Fichter. 120 pp. Price, 33 mk. F. Enke, Stuttgart.

Research in Industry: The Basis of Economic Progress. Arthur Percy, M. Fleming and J. G. Pearce. 244 pp. Illustrated. Price, $4.00. Isaac Pitman & Sons, New York.

Science in the Service of Man. Electricity. S. G. Starling. 245 pp. Price, 10s. 6d. net. Longmans, Green & Co., London.

Soap: Nouveau Traité Théorique et Pratique de Savonnerie. J. Fritsch. 580 pp. Illustrated. Price, 48 fr. Dunod, Paris.

Teaching of General Science. William Lewis Eikenberry. 169 pp. Price, $2.00. University of Chicago Press, Chicago.

Textiles: La Chimie dans l'Industrie Textile; Matières Colorantes Artificielles, leur Fabrication et leur Emploi. Henri Vassart. 238 pp. Price, 30 fr. Albin Michel, Paris.

Textiles: Analysis of Woven Fabrics. Aldred F. Barker and Eber Midgley. 2nd revised and enlarged edition. 337 pp. Illustrated. Price, $5.00. D. Van Nostrand Co., New York.

Vegetable Oil Industry in the Bombay Presidency. A. F. Yuill. 95 pp. Price, Rs. 1–13–0. Government Central Press, Poona, Bombay.

RECENT JOURNAL ARTICLES

Aluminium: Influence of Cerium on Aluminium and Other Light Metal Alloys. Josef Schulte. *The Metal Industry*, Vol. **20** (1922), No. 4, pp. 142–44. Translated from *Metall und Erz.*

Ammonia: The Thermal Dissociation of Ammonia with Special Reference to Coke Oven Conditions. G. E. Foxwell. *Journal of the Society of Chemical Industry*, Vol. **41** (1922), No. 8, pp. 114*t*–25*t*.

Artificial Disintegration of the Elements. Sir Ernest Rutherford. *Journal of the Chemical Society*, Vol. **121** (1922), No. 713, pp. 400–15.

Asbestos Milling and Mining in Quebec. Walter A. RuKeyser. *Engineering and Mining Journal-Press*, Vol. **113** (1922), No. 15, pp. 617–25; No. 16, pp. 670–77.

Atomic Weights and Isotopes. F. W. Aston. *Journal of the Franklin Institute*, Vol. **193** (1922), No. 5, pp. 581–608.

Carborundum Brick. M. F. Peters. *Journal of the American Ceramic Society*, Vol. **5** (1922), No. 4, pp. 181–208.

Chemical Research and Textile Industry. Frederick Albert Hayes. *Textile World*, Vol. **61** (1922), No. 16, pp. 31–33.

Colloids: The Transition from Crystalloid to Colloid Properties within Homologous Series. Edgar J. Witzemann. *Journal of Physical Chemistry*, Vol. **26** (1922), No. 3, pp. 201–16.

Color in Relation to Dyeing. J. Merritt Matthews. *Color Trade Journal*, Vol. **10** (1922), No. 5, pp. 183–88.

Color: The Standardization of Colors. H. Trillich. *Color Trade Journal*, Vol. **10** (1922), No. 5, pp. 194–97. Translated from *Farbenzeitung.*

Combustion of Complex Gaseous Mixtures. William Payman and Richard Vernon Wheeler. *Journal of the Chemical Society*, Vol. **121** (1922), No. 713, pp. 363–79.

Copper: Heap Leaching of Low-Grade Copper Ores. I. Joseph Irving. *Engineering and Mining Journal-Press*, Vol. **113** (1922), No. 17, pp. 714–21.

Copper: Sulfatizing Roasting of Semi-Oxidized Copper Ores. Percy R. Middleton. *Engineering and Mining Journal-Press*, Vol. **113** (1922), No. 15, pp. 629–31.

Corrosion: Control of Corrosion by Deactivation of Water. Frank N. Speller. *Journal of the Franklin Institute*, Vol. **193** (1922), No. 4, pp. 515–42.

Drop Forgings: The Testing of Drop Forgings. Leslie Aitchison. *Forging and Heat Treating*, Vol. **8** (1922), No. 4, pp. 188–92. Reprinted from *The Drop Forger.*

Flash Point: The Physicochemical Significance of Flash-Point Temperatures. W. R. Ormandy and E. C. Craven. *The Chemical Trade Journal and Chemical Engineer*, Vol. **70** (1922), No. 1808, pp. 41–42.

Gas: On the Removal of Naphthalene. O. L. Kowalke and A. W. Pesch. *American Gas Journal*, Vol. **116** (1922), No. 15 (whole no. 3345), pp. 347–49, 354–55.

German Chemical Industry: L'État Actuel de la Grande Industrie Chimique Allemande. M. Kaltenbach. *Chimie et Industrie*, Vol. **7** (1922), No. 3, pp. 419–24.

Fire Brick: Resistance Tests on Fire Bricks under Loads at High Temperatures. E. Sieurin and Fredr. Carlsson. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 4, pp. 170–80.

Mannite: Sulla Fabbricazione della Mannite. Piero Fenaroli. *Giornale di Chimica Industriale ed Applicata*, Vol. 4 (1922), No. 3, pp. 85–89.

Optical Glass: Pots Used in Optical Glass Manufacture. R. J. Montgomery and M. R. Scott. *The Glass Industry*, Vol. 3 (1922), No. 5, pp. 91–93.

Paint: La Chimie des Peintures en Batiment et son Évolution Scientifique. Paul Razous. *L'Industrie Chimique*, Vol. 9 (1922), No. 98, pp. 103–05.

Photosynthesis and the Functions of Pigments in the Living Plant. E. C. C. Baly. *Journal of the Society of Dyers and Colourists*, Vol. 38 (1922), No. 1, pp. 4–9.

Potassium: La Production de la Potasse et de l'Alumine à Partir des Leucites Italiennes au Moyen du Chlore. Umberto Pomilio. *Chimie et Industrie*, Vol. 7 (1922), No. 3, pp. 425–37.

Pressure-Volume Relation of Superheated Liquids. K. L. Wismer. *Journal of Physical Chemistry*, Vol. 26 (1922), No. 4, pp. 301–15.

Steel: Ball Bearing Steel and Its Heat Treatment. Carl T. Hewitt. *Forging and Heat Treating*, Vol. 8 (1922), No. 4, pp. 196–98.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

Cement Industry of China. J. M. Clements. *Trade Information Bulletin* 7; Far Eastern Division. 8 pp. 1922.

Bureau of Mines

Acetylene as a Precipitant for Cyanide Solutions. John Gross. *Reports of Investigations* **2346.** 2 pp. Issued April 1922.

Bibliography of Articles Relating to the Preservation of Mine Timber 1921. R. R. Hornor. *Reports of Investigations* **2343.** 6 pp. Issued April 1922.

Evaporation Loss of Petroleum in the Mid-Continent Field. J. H. Wiggins. *Bulletin* **200.** 115 pp. Paper, 20 cents.

Explosives Used in March 1922. W. W. Adams. *Reports of Investigations* **2353.** 4 pp. Issued May 1922.

Fatalities at Coal Mines in February 1922. W. W. Adams. *Reports of Investigations* **2334.** 4 pp. Issued March 1922.

Preparation and Uses of Tar and Its Simple Crude Derivatives. W. W. Odell. *Technical Paper* **268.** 84 pp. Paper, 15 cents. This report was prepared under a coöperative agreement with the Illinois State Geological Survey and the Department of Mining Engineering of the University of Illinois.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. *Reports of Investigations* **2340.** 29 pp. Issued March 1922.

Survey of Pacific Coast Petroleum Products. E. C. Lane. *Reports of Investigations* **2342.** 7 pp. Issued April 1922.

Bureau of Standards

An Improved Method for Preparing Raffinose. E. P. Clark. *Scientific Paper* **432.** Paper, 5 cents.

How to Get Better Service with Less Natural Gas in Domestic Gas Appliances. *Circular* **116** (Reprint). 7 pp. Paper, 5 cents.

Congress

Fertilizers. A bill to provide for the manufacture of explosives for the use of the Army and Navy, to provide for the manufacture of fertilizer for agricultural purposes, to incorporate the Federal Chemical Corporation, and for other purposes. S. 3420. Introduced by Mr. Norris, April 10, 1922; read twice and referred to the Committee on Agriculture and Forestry. 10 pp.

Patents. A bill to amend Section 4886 of the Revised Statutes relating to patents. S. 3410. Introduced by Mr. Stanley, April 5, 1922; read twice and referred to the Committee on Patents. 3 pp.

Congressional Committees

Muscle Shoals. Digest of the Statements made on Muscle Shoals Propositions at the Hearings before the Committee on Military Affairs of the House of Representatives, February 8, 1922, to March 13, 1922. 44 pp.

Hearings before the Committee on Agriculture and Forestry of the United States Senate on S. 3420, to provide for the manufacture of explosives for the use of the Army and Navy, to provide for the manufacture of fertilizer for agricultural purposes, to incorporate the Federal Chemical Corporation, and for other purposes and on the Henry Ford Muscle Shoals offer; offer made by the Alabama Power Co., proposing to complete Wilson Dam; offer of Frederick E. Engstrum for Muscle Shoals; and offer of Charles L. Parsons for properties at Muscle Shoals, Ala. February 16, April 10, 12, and 13, 1922. Part I. 96 pp.

Hearings before the Committee on Military Affairs, House of Representatives, February 9, 1922, to March 13, 1922. In one volume. 1208 pp.

Scientific Investigators, etc., Department of Agriculture. Report to accompany H. R. 10819 relating to salaries of employees engaged in scientific work and to appropriations of the Department of Agriculture; submitted by Mr. Haugen. H. Rpt. 785. 2 pp.

Department of Agriculture

Comparison of Corn Oils Obtained by Expeller and Benzene Extraction Methods. A. F. Sievers. *Department Bulletin* **1054.** 20 pp. Paper, 5 cents.

Poisonous Metals on Sprayed Fruits and Vegetables. W. D. Lynch, C. C. McDonnell, J. K. Haywood, A. L. Quaintance and M. B. Waite. *Department Bulletin* **1027.**

Pulpwood Consumption and Wood Pulp Production, 1920. R. V. Reynolds and A. H. Pierson. New York, American Paper and Pulp Association. Prepared in coöperation with the American Paper and Pulp Association. 39 pp.

Report on Drainage and Prevention of Overflow in the Valley of the Red River of North. P. T. Simons and F. V. King. *Department Bulletin* **1017.** 89 pp. Paper, 50 cents. 1922.

Sorghum-Sirup Manufacture. A. H. Bryan. Revised by C. S. Hudson and S. F. Sherwood. *Farmers' Bulletin* **477.** 38 pp. Paper, 5 cents.

The Chaulmoogra Tree and Some Related Species. A Survey Conducted in Siam, Burma, Assam, and Bengal. J. F. Rock. With an introductory chapter by David Fairchild and a chapter on the chemistry of chaulmoogra, hydnocarpus, and gynocardia oils by F. B. Power. *Department Bulletin* **1057.** 29 pp. Paper, 15 cents. Published April 24, 1922.

The Manufacture of Ethyl Alcohol from Wood Waste. F. W. Kressman. *Department Bulletin* **983.** 100 pp. Published April 6, 1922.

The Preparation of an Edible Oil from Crude Corn Oil. A. F. Sievers and J. H. Shrader. *Department Bulletin* **1010.** 25 pp. Paper, 5 cents. Published April 3, 1922.

Geological Survey

Bonanza Ores of Comstock Lode, Virginia City, Nevada. E. S. Bastin. *Bulletin* **735-C.** 63 pp.

Cadmium in 1921. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1921, Part I. 5 pp. Published April 10, 1922.

Gold, Silver, Copper, and Lead in Alaska in 1920. Mines Report. A. H. Brooks. Separate from Mineral Resources of the United States, 1920, Part I. 6 pp. Published April 24, 1922.

Lead and Zinc Pigments and Salts in 1920. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1920, Part I. 4 pp. Published April 26, 1922.

Mica in 1920. B. H. Stoddard. Separate from Mineral Resources of the United States, 1920, Part II. 5 pp. Published April 12, 1922.

Natural-Gas Gasoline in 1920. E. G. Sievers. Separate from Mineral Resources of the United States, 1920, Part II. 12 pp. Published April 28, 1922.

Ore Deposits of Sierrita Mountains, Pima County, Arizona. F. L. Ransome. *Bulletin* **725-J.** 4 pp.

Sulfur and Pyrites in 1919. P. S. Smith. Separate from Mineral Resources of the United States, 1919, Part II. 12 pp. Published April 29, 1922.

The Arkansas River Flood of June 3-5, 1921. Robert Follansbee and E. E. Jones. *Water-Supply Paper* **487.** Paper, 10 cents. 1922.

Tin in 1920. B. L. Johnson. Separate from Mineral Resources of the United States, 1920, Part I. 5 pp. Published April 27, 1922.

Public Health Service

A Survey of Natural Illumination in an Industrial Plant. With Special Reference to the Use of the Indoor-Outdoor Ratio in Establishing Standards of Daylight Illumination. C.-E. A. Winslow and Leonard Greenburg. *Public Health Reports* **37** (April 14, 1922), 876–87.

The Comparative Antiscorbutic Values of Milk. J. M. Johnson and C. W. Hooper. *Public Health Reports* **37** (April 28, 1922), 989–1021.

Tariff Commission

Summary of Tariff Information 1921. Relative to the Bill H. R. 7456. 1625 pp. Paper, $1.25. 1922.

Tariff Information Surveys. Revised edition, 1922. FL-35. On articles in paragraphs 631–637 of Tariff Act of 1913 and related articles in other paragraphs. Tin. 15 pp. Paper, 10 cents.

MARKET REPORT—MAY, 1922

[Supplied by Drug & Chemical Markets]

April and May saw a decided increase in the activity of the heavy chemical market. The attitude of consumers has been gradually changing from one of timidity in the face of possible price declines to one of increasing confidence. Not only is this true of American buyers but of foreign buyers as well, and has reflected itself in all chemical markets. During this period advances have been announced on many imported products which have been sufficient to turn much of the business of chemical importers into the hands of domestic manufacturers. The cause of these advances seems to be increased activity on the part of continental buyers as well as those in South America and Japan. Undoubtedly the prospect of higher duties on most imports is exerting some influence on exporters abroad and is tending to increase the firmness of their prices to us.

In the domestic situation, the coal and textile strikes are considered highly important from the market standpoint. Coal-tar distillates have been scarce and very firm for months past for two primary reasons. The motor fuel industry has absorbed large quantities of the lighter distillates, which they can use in a less refined state than that required by the chemical manufacturers, and no surplus of these materials, benzene, toluene, and xylene, has been allowed to accumulate. The limited activity of the iron and steel industry has necessarily held the activity of the coke ovens at a minimum, and, now that the furnaces are being put into blast again, supplies of coal are dwindling on account of the miners' strike.

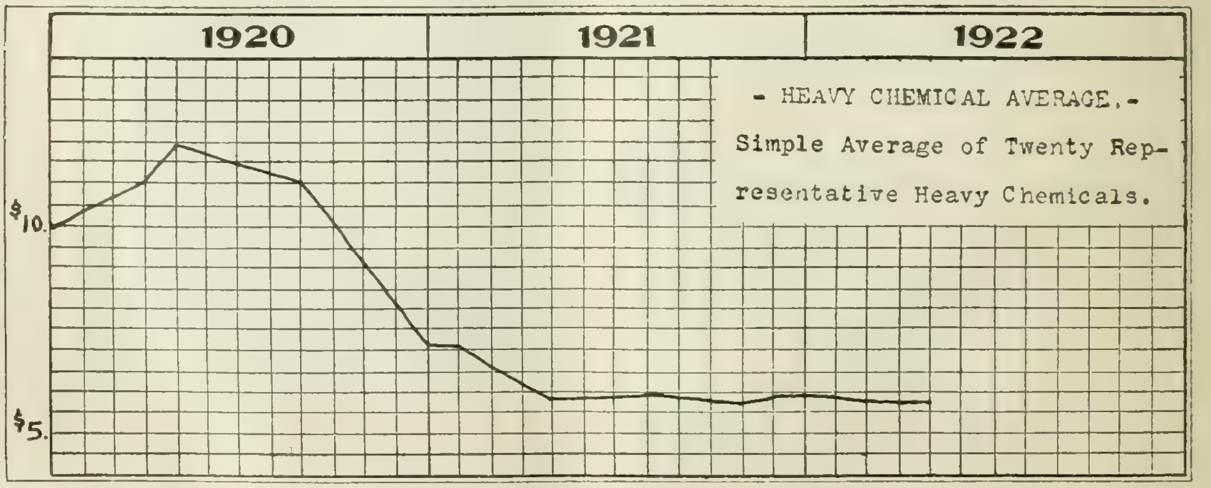
The New England textile districts are almost completely tied up by the strike of the textile workers there, and their ordinarily heavy consumption of chemical products has been reduced to a minimum. Stocks in their warehouses are practically nil, certainly not large enough to cover a week's requirements. In the meantime the strikers are becoming more and more anxious to get back to work. It is generally believed now that not less than 75% of the strikers would return to work immediately if the mills were opened. However that may be, there is expected to be a more or less sudden increase in the requirements of the mills on opening which will force even greater firmness into a market which is practically bare of stocks. This extreme effect will probably be only temporary, however, on account of the fact that makers are expected to be able to get into operation easily within a week.

Price fluctuations in heavy chemicals were rather widely distributed. Barium chloride rose sharply late in April but settled to the American makers' level in May. Caustic soda in the resale market advanced on increased export demand. At the same time decided weakness developed in all chlorine products, especially bleaching powder. Prussiates of soda and potash have recovered from their recent weakness and appear to be due for further advances. Nitrogenous fertilizers are weaker. Metal prices are generally firmer.

Medicinal chemicals have moved more slowly but prices in this section of the market are held firm. The first two weeks of May witnessed distinct falling off in demand for which no definite cause has been assigned. Both manufacturers and importers have refused to be stampeded into price concessions, but on the contrary are generally quoting slightly higher.

Demand for coal-tar products has been very slow and sales have generally been made at concessions. Price cutting in aniline oil and beta-naphthol has become very serious and present quotations are said to be below production costs. Competition in para-nitroaniline following the entrance of a new maker into the field may reach serious proportions. Strictly prime white U. S. P. phenol is scarce and closely held although government surplus of stocks of slightly colored stuff are still available in good quantity. Benzene and toluene are very firm from refiners with stocks held very low. Naphthalene is comparatively soft with only scattered demand.

Oils have continued their steady advance started nearly a year ago but the actual amount of business transacted has been of a rather limited nature. Linseed oil has been advancing on the prospect of the tariff and lower prices on oil cake and meal. Importers of linseed oil have been forced to advance their prices proportionately and continue to receive large shipments of foreign oil. Cottonseed oil is scarce, but steady on light routine demand. Fish oils are scarce, particularly menhaden and cod oils. Perilla and teaseed oils from the Orient are attracting much more attention here. Turpentine has fluctuated widely but shows little net change. Rosin prices are lower.



Courtesy of Drug & Chemical Markets

FIRST HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

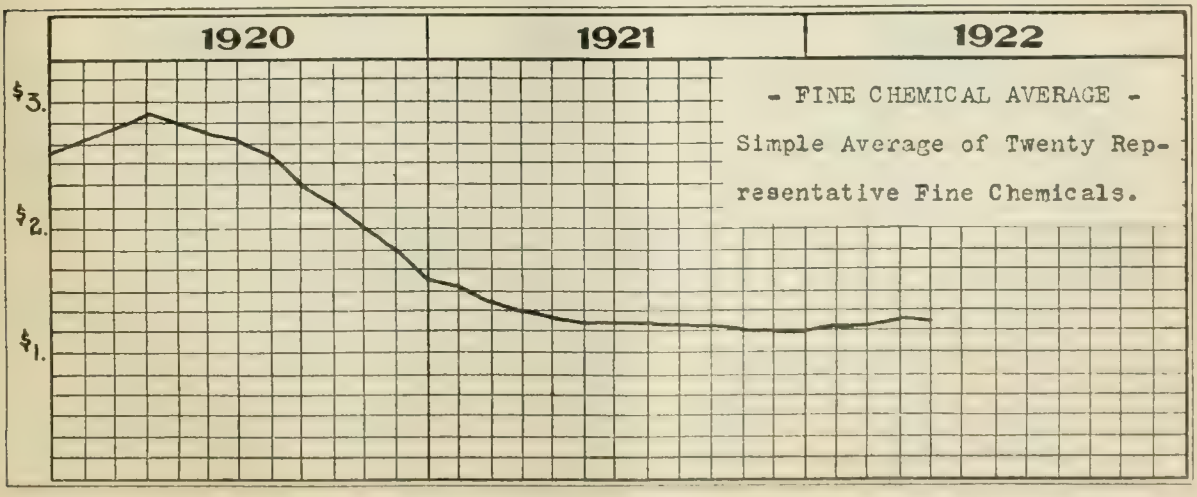
	May 1	May 15	Jan. 1922
Acid, Boric, cryst. bbls.......lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l 20°.lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.06	.06	.06
Phosphoric, 50% tech.....lb.	.08	.08	.10
Sulfuric, C. P............lb.	.07	.07	.07
66° tks. wks.........ton	16.00	16.00	16.00
Oleum 20%.........ton	19.00	19.00	19.00
Alum, Ammonia, lump........lb.	.03½	.03½	.03½
Potash, lump............lb.	*.03½	*.03½	*.03½
Chrome.............lb.	.06½	.06½	.07
Soda, ground............lb.	.03½	.03½	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.07	.07	.08
Chloride, white gran......lb.	.07¾	.07¾	.07½
Ammonia, anhydrous ....lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.06¾	.07¼	.06½
Barium Chloride............ton	*105.00	*100.00	*53.00
Nitrate.................lb.	*.06	*.06	*.07
Barytes, white..............ton	28.00	28.00	28.00
Bleaching Powd., 35%, works ....100 lbs.	1.60	1.60	2.25
Borax, cryst., bbls............lb.	.05½	.05½	.05¾
Bromine, pure, wks...........lb.	.23	.23	.20
Calcium Chloride, fused, f.o.b. N. Y.................ton	24.50	24.50	28.75
Chlorine, liquid..............lb.	.06	.06	.06
Copper Sulfate..........100 lbs.	5.50	5.50	5.55
Iodine, resublimed...........lb.	4.05	4.20	3.80
Lead Acetate, white crystals...lb.	.11	.11	.11
Nitrate.................lb.	.15	.15	.15
Red.....................lb.	.08	.08	.08
White (Carb.)............lb.	.07¼	.07¼	.07¼
Lime Acetate...........100 lbs.	1.75	1.75	1.75
Magnesium Carbonate, tech...lb.	.06	.06	.06
Magnesite, calcined..........ton	30.00	30.00	30.00
Phosphorus, yellow...........lb.	.25	.25	*.27
Red.....................lb.	*.26	*.26	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate........lb.	.10	.10	.10½
Bromide, imported.......lb.	*.16	*.16½	*.13
Carbonate, calc., 80–85%.lb.	*.04½	*.04¾	*.04½
Chlorate, cryst...........lb.	*.06½	*.06½	*.05½
Hydroxide, 88–92%......lb.	*.06	*.06	*.06
Iodide, bulk.............lb.	3.15	3.30	2.90
Nitrate.................lb.	.08	.08	.08
Permanganate, U. S. P....lb.	*.14	*.14	*.15
Prussiate, red............lb.	*.85	*.85	*.29
Yellow..............lb.	*.27½	*.30	*.24½
Salt Cake, bulk..............ton	21.00	21.00	17.00
Silver Nitrate...............oz.	.45½	.48	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.65	3.90	3.80

*Resale or Imported (not an American makers' price).

	May 1	May 15	Jan. 1922
Sodium Acetate..........lb.	.04	.04	.04
Bicarbonate.......100 lbs.	2.00	2.00	2.00
Bichromate..............lb.	.07¼	.07¼	.07¾
Bisulfite, powd...........lb.	.04¼	.04¼	.04¼
Chlorate.................lb.	.06¾	.06¾	.07½
Cyanide, 96–98%........lb.	.25	.25	.28
Fluoride, tech............lb.	.10	.10	.09½
Hyposulfite, bbls.....100 lbs.	3.25	3.25	3.50
Nitrate, 95%.......100 lbs.	2.85	2.80	2.32½
Nitrite..................lb.	.09½	.09½	.06½
Prussiate, yellow.........lb.	.17½	.20	.16½
Phosphate (di-sod.),tech..lb.	.04	.04	.04¼
Silicate, 40°.............lb.	.01	.01	.01⅛
Sulfide, 60%, fused.......lb.	.04	.04	.05
Strontium Nitrate............lb.	*.08	*.08	*.10
Sulfur, flowers...........100 lbs.	3.00	3.00	2.75
Crude, mines.......long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n......lb.	.10½	.10½	.09¾
Oxide...................lb.	.37	.38	.37
Zinc Chloride, U. S. P.........lb.	.35	.35	.35
Oxide, bbls..............lb.	.08	.08	.08

ORGANIC CHEMICALS

	May 1	May 15	Jan. 1922
Acetanilide, U. S. P. bbls.......lb.	*.31	*.30	*.29
Acid, Acetic, 28 p. c.......100 lbs.	2.37½	2.37½	2.37½
Glacial..............lb.	.08	.08	.10
Benzoic, U. S. P.........lb.	.55	.55	.60
Carbolic, cryst., U. S. P., drs...............lb.	.14	.14	.12
50- to 110-lb. tins....lb.	.19	.19	.18
Citric, crystals, kegs......lb.	*.45	*.44½	*.43
Oxalic, cryst., bbls., wks...lb.	.11½	.13½	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.........lb.	.26	.26	.24
Tannic, U. S. P., bbls....lb.	.60	.60	.75
Tartaric, cryst., U. S. P...lb.	*.26½	*.27	*.25
Acetone, drums..............lb.	.08	.08	.12
Alcohol, denatured, complete.gal.	.30	.27	.45
Ethyl, 190 proof, bbls....gal.	4.65	4.65	4.75
Amyl Acetate...............gal.	1.90	1.90	2.00
Camphor, Jap, refined, cases...lb.	.78	.77	.90
Carbon Bisulfide, c/l..........lb.	.06	.06	.06½
Tetrachloride............lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.38	.30	.43
Creosote, U. S. P.............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.12	.12	.14
Dextrin, corn...........100 lbs.	2.99	2.94	2.70
Imported Potato.........lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs.........lb.	.14	.14	.14
Formaldehyde, bbls...........lb.	.08½	.08	.10½
Glycerol, dynamite, drums....lb.	.13	.12½	.14½
Methanol, pure, bbls.........gal.	.72	.72	.75
Methylene Blue, med........lb.	3.50	3.50	4.00
Petrolatum, light amber......lb.	.04½	.04½	.05¼
Pyridine...................gal.	1.75	1.75	1.75
Starch, corn, pow'd......100 lbs.	2.32	2.32	2.13
Potato, Jap..............lb.	.07	.07	.06½
Sago....................lb.	.03½	.03½	.04



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	May 1	May 15	Jan. 1922
Beeswax, pure, white ....lb.	.33	.35	.33
Castor Oil, No. 3.............lb.	.11	.11	.10½
Ceresin, yellow..............lb.	.07½	.07½	.07½
Corn Oil, crude, tanks, mills...lb.	.09½	.09½	.06¾
Cottonseed Oil, crude, f. o. b. mill.....................lb.	.10	.10	.07
Linseed Oil, raw, c/l.........gal.	.88	.90	.69
Menhaden Oil, crude, mills...gal.	.40	.40	.35
Neat's-foot Oil, 20°..........lb.	.24	.24	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	5.35	5.50	5.30
Rosin Oil, first run..........gal.	.36	.36	.36
Shellac, T. N................lb.	.78	.73	.66
Sperm Oil, bleached winter, 38°..................gal.	1.69	1.69	1.70
Stearic Acid, double pressed...lb.	.09½	.09½	.09¾
Tallow Oil, acidless..........lb.	.10	.10	.10
Turpentine, spirits of........gal.	.92	.91	.82½

METALS

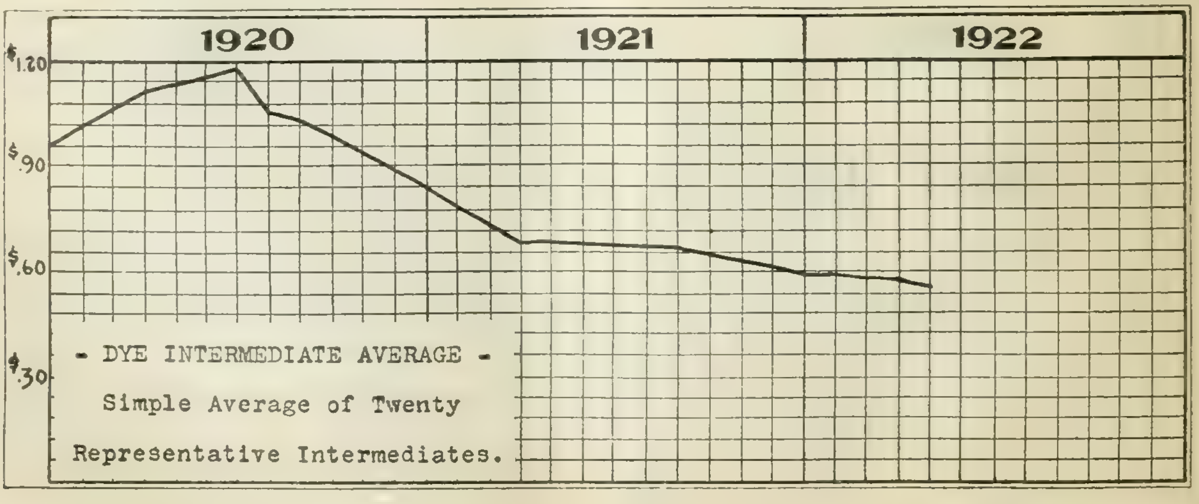
	May 1	May 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.17½	.17½	.17
Antimony, ordinary......100 lbs.	5.30	5.37½	4.55
Bismuth......................lb.	2.10	2.10	1.80
Copper, electrolytic..........lb.	.12⅞	.13⅛	.13⅞
Lake...................lb.	.12⅞	.13⅛	.13¾
Lead, N. Y..............100 lbs.	5.45	5.35	4.70
Nickel, electrolytic...........lb.	.39	.39	.45
Platinum, refined, soft........oz.	90.00	90.00	78.00
Quicksilver, flask......75 lbs. ea.	55.00	55.00	52.00
Silver, foreign...............oz.	.68⅜	.72⅛	.65¼
Tin..........................lb.	.31	.30⅝	.32¾
Tungsten Wolframite....per unit	2.00	2.00	2.00
Zinc, N. Y..............100 lbs.	5.30	5.45	5.20

FERTILIZER MATERIALS

	May 1	May 15	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.60	3.50	2.60
Blood, dried, f. o. b. N. Y....unit	3.65	3.65	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks......unit	3.50 & .10	3.50 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%......ton	6.00	6.00	8.00
Potassium Muriate, 80%....unit	*.60	*.60	*.75
Tankage, high-grade, f. o. b. Chicago...............unit	3.65 & .10	3.65 & .10	3.00 & .10

COAL-TAR CHEMICALS

	May 1	May 15	Jan. 1922
Crudes			
Anthracene, 80–85%........lb.	.75	.75	.75
Benzene, pure, tanks ....gal.	.29	.29	.29
Naphthalene, flake...........lb.	.06½	.06½	.07½
Phenol, drums...............lb.	.12	.12	.11
Crudes (*concluded*)			
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks..................gal.	.45	.45	.45
Intermediates			
Acids:			
Anthranilic..............lb.	1.10	1.10	1.10
Benzoic, tech............lb.	.50	.50	.50
Cleve's..................lb.	1.50	1.50	1.50
Gamma...................lb.	1.80	1.80	2.25
H.......................lb.	.85	.85	1.00
Metanilic................lb.	1.00	1.00	1.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.60	.60	.65
Nevile & Winther's.......lb.	1.25	1.25	1.30
Picric...................lb.	.20	.20	.25
Sulfanilic................lb.	.22	.22	.26
Tobias'..................lb.	1.50	1.50	2.00
Aminoazobenzene..........lb.	1.15	1.15	1.15
Aniline Oil.................lb.	.15	.14	.17
Aniline Salt................lb.	.22	.20	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech...........lb.	.65	.65	.45
U. S. P.................lb.	1.40	1.40	1.25
Benzidine Base..............lb.	.85	.85	.90
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol..............lb.	5.50	5.50	5.50
Dianisidine.................lb.	4.50	4.50	4.75
p-Dichlorobenzene..........lb.	.17	.17	.15
Diethylaniline...............lb.	.60	.60	.90
Dimethylaniline.............lb.	.36	.36	.40
Dinitrobenzene..............lb.	.20	.20	.21
Dinitrotoluene..............lb.	.20	.20	.25
Diphenylamine..............lb.	.58	.58	.58
G Salt......................lb.	.65	.65	.70
Hydroquinol................lb.	1.10	.90	1.35
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline ....lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.28	.25	.30
a Naphthylamine ....lb.	.30	.30	.30
b-Naphthylamine............lb.	.95	.95	1.05
m-Nitroaniline...............lb.	.72	.72	.85
p-Nitroaniline...............lb.	.75	.75	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	.75	.75	.75
o-Nitrotoluene..............lb.	.12	.12	.15
p-Nitrotoluene..............lb.	.60	.60	.70
m-Phenylenediamine.........lb.	1.00	1.00	1.10
p-Phenylenediamine..........lb.	1.50	1.50	1.60
Phthalic Anhydride..........lb.	.35	.35	.38
R Salt ....lb.	.55	.55	.60
Resorcinol, tech.............lb.	1.30	1.30	1.50
U. S. P.................lb.	1.75	1.75	2.00
Schaeffer's Salt. ....lb.	.60	.60	.70
Sodium Naphthionate........lb.	.60	.60	.70
Thiocarbanilide..............lb.	.35	.35	.40
Tolidine (base)..............lb.	1.15	1.15	1.20
Toluidine, mixed............lb.	.30	.30	.30
o-Toluidine.................lb.	.16	.16	.20
p-Toluidine.................lb.	1.00	1.00	1.10
m-Toluylenediamine.........lb.	.95	.95	1.10
Xylidine....................lb.	.42	.42	.40



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